SURFACE FORCES Studied With Colloidal Probe Atomic Force Microscopy

Promotoren: prof. dr. M.A. Cohen Stuart hoogleraar in de Fysische Chemie, met bijzondere aandacht voor de Kolloïdchemie

> prof. dr. G.J. Fleer persoonlijk hoogleraar bij de leerstoelgroep Fysische Chemie en Kolloïdkunde

Co-promotor: dr. ir. J.M. Kleijn universitair docent bij de leerstoelgroep Fysische Chemie en Kolloïdkunde

Samenstelling promotiecommissie:

prof. dr. J. Lyklema	(Wageningen Universiteit)
prof. dr. E.J.R. Südholter	(Wageningen Universiteit)
prof. dr. G. Frens	(Technische Universiteit Delft)
dr. R.A. Hayes	(Philips Natuurkundig Laboratorium Eindhoven)

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Marcel Giesbers

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Marcel Giesbers

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- De bewering van Ederth et al dat de wisselwerking tussen twee silica deeltjes van enkele micrometers groot bedekt met een goudlaagje van circa 10 nm dik vrijwel gelijk is aan die tussen twee onbedekte silica deeltjes is onjuist.
 T. Ederth, P. Claesson, B. Liedberg, Langmuir, 14 (1998) 4782 Dit proefschrift, hoofdstuk 3
- Stromingspotentiaalmetingen zijn geschikt om de zeta-potentiaal van geleidende materialen als goud te bepalen. Dit proefschrift, hoofdstuk 3
- 3. In tegenstelling tot wat Luckham *et al* rapporteren reikt de interactie tussen twee met polymeer (poly (ethyleenoxide)) bedekte oppervlakken niet verder dan twee maal de gyratiestraal van het polymeer.

J. Klein, P. F. Luckham, Macromolecules, 17 (1984) 1041; G. J. C. Braithwaite, P. F. Luckham, J. . Chem. Soc. Faraday Trans., 93 (1997) 1409 Dit proefschrift, hoofdstuk 4

- 4. Bij de beschouwing van de oppervlaktekrachten tussen kolloïdale deeltjes wordt ten onrechte aan oppervlakteruwheid weinig of geen aandacht besteed. Dit proefschrift, hoofdstuk 5
- 5. De elektrostatische wisselwerking tussen oppervlakken met gelijk ladingsteken maar ongelijke wandpotentiaal is niet monotoon. De bestaande theorie voor deze wisselwerking is niet instaat de experimentele resultaten kwantitatief te beschrijven. *Dit proefschrift, hoofdstuk 3 & 5*
- 6. Rupert Sheldrake's theorie over morfogenetische velden (1981) vertoont erg veel overeenkomsten met Jung's theorie over het collectief onbewuste (1936). Rupert Sheldrake, A New Science of Life, Inner Traditions Int. Ltd. Carl Gustaf Jung, "The Archetypes and the Collective Unconscious", Collected Works, Vol. 9.1, Princeton Univ Press
- 7. De snel toenemende lichtvervuiling in de geïndustrialiseerde landen zal de nachtelijke sterrenhemel voor komende generaties voorgoed doen verbleken.
- 8. Het SETI@home project is een prima voorbeeld van participatie van leken in het onderzoek.

- Thuiswerken via het internet is waarschijnlijk de enige manier om het fileprobleem op te lossen. Daarom is het investeren in de digitale snelweg beter te verantwoorden dan het investeren in tolpoorten en spitsstroken.
- Getuige de discussie rond de millenniumwisseling is de kunst van het tellen er in een paar honderd jaar niet op vooruit gegaan. The Times, 26 December 1799
- 11. Daar 'internet' en 'world wide web' voor het merendeel van de mensen synoniemen zijn geworden is het gebruik van www in internetadressen volledig overbodig geworden en leidt dit tot eenzijdige slijtage van het toetsenbord.
- 12. De groeiende groep van computergebruikers op de wereld maakt gebruik van een steeds beperktere set programma's op machines van vrijwel dezelfde architectuur. Zo'n monocultuur is extreem gevoelig voor parasieten. Dat de parasieten op eenvoudige manier te maken zijn en verspreiding ervan door het internet zeer snel kan zijn creëert een doomsday scenario. Hier geldt: compudiversiteit is een voorwaarde om te overleven.

Stellingen behorende bij het proefschrift Surface Forces Studied With Colloidal Probe Atomic Force Microscopy door Marcel Giesbers in het openbaar te verdedigen op maandag 22 Januari 2001

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Chapter 1

Introduction

1.1 General introduction

When studying a colloidal system, for instance a sol (a colloidal dispersion of particles in a liquid), we soon find out that forces are very important and that the mere existence of such a colloidal system depends on the balance of a number of forces. The force that we are all most familiar with, gravity, also works on particles dispersed in a liquid. Therefore, we would expect dense particles to sink to the bottom of the vessel. However, the particles of a colloidal dispersion are so small that the continuous bombardment by molecules of the liquid is sufficient to keep them dispersed. The resulting random motion of the particles is called *Brownian motion*¹. In this example at least already three forces are working on the colloidal particles. Firstly, gravitation (Sir Isaac Newton, 1687)[1]. Secondly, a force caused by the Brownian collisions. The kinetic energy of the collisions depends on the temperature and is of order kT (with k Boltzmann's constant and T the absolute temperature). Thirdly, an upward force equal to the weight of the displaced liquid (Archimedes, around 250 Bc)[2].

There are also forces acting *between* the particles. These forces are even more important with regard to the stability of the colloidal dispersion. When particles attract each other, collisions between them lead to aggregates which will grow so large that they cannot be kept in solution by Brownian motion. As a result these aggregates will eventually settle. However, when the particles repel each other the system will remain unchanged as collisions between particles will not give rise to aggregation.

Between particles of equal composition one of the forces acting is always attractive. This attraction is the result of the fact that the electron clouds in two atoms (or molecules) at short distance are correlated in such a way that at any time one atom (or molecule) induces a dipole moment on the other. When two colloidal particles are brought close the mutual interactions between their constituting atoms lead to an attraction. The magnitude of this *dispersion force* or *Van der Waals force* (Johannes Diderik van der Waals, 1873) [3] depends on many factors, but roughly speaking the

¹ This phenomenon was discovered by Robert Brown, a British botanist, and is therefore referred to as *Brownian motion*.

Chapter 1

attractive energy is of order kT for a separation distance of one particle diameter. At shorter distances it is, of course, larger.

If this Van der Waals force would be the only force acting between the particles, they would surely aggregate. Two mechanisms, however, can prevent aggregation and stabilise the colloidal system. The first is *electrostatic repulsion:* if the particles carry the same electric charge they will repel each other and if this repulsion is high enough to prevent the particles to come close, aggregation will not occur. The stability of lyophobic colloids is described by the DLVO theory, named after Derjaguin, Landau, Verwey, and Overbeek [4, 5]. In this theory the interaction between colloidal particles in aqueous solution is modelled by taking into account Van der Waals forces and electrostatic forces.

A second possible mechanism is *steric stabilisation*. In this case, typically a layer of adsorbed polymer, is present around the particles. This layer prevents the particles to come close, keeping them apart far enough to make the Van der Waals attraction too small to play a significant role.

Forces between surfaces, often denoted, for short, as *surface forces*, determine the behaviour of a great variety of materials. These forces dictate the interactions between colloidal particles and the interactions between colloidal particles and (macroscopic) surfaces. They are of crucial importance in both natural and synthetic systems. For instance, the structure (and possibility of cultivation) of soils is to a large degree determined by the interactions between clay, sand and other particles. Physiological processes are dominated by interactions between protein molecules and membrane systems. In industry knowledge of and control over surface forces is essential, for example, in the production of particle layers on macroscopic surfaces. Such layers are used in many applications, such as the production of protective coatings, television and computer screens, and fluorescent lamps. For easy handling and for obtaining homogeneous layers the colloidal dispersion used in these production processes should be stable; on the other hand, for good adhesion to the surface, attraction between particles and surface is necessary.

Besides the type of forces already mentioned we can distinguish several other surface forces. *Hydrophobic interactions* between hydrophobic surfaces in aqueous medium are attractive interactions generally of longer range than Van der Waals interactions. The origin of these interactions is still not clearly understood and under debate, although there is consensus that the phenomenon is dominated by the strong self-association of water molecules which try to avoid non-polar solutes and surfaces.

The presence of adsorbing polymers may lead to steric repulsion as mentioned earlier, but can also give rise to *bridging forces*, *i.e.*, attractive interactions caused by polymers adsorbed on one surface bridging the gap to the other surface.

In solutions of nonadsorbing polymers *depletion* is encountered. This force arises as the distance between two opposing surfaces approaches the dimensions of the polymer coils: these then become excluded from the volume between the two surfaces and this concentration imbalance creates a net attractive osmotic force, the depletion force.

Structural forces originate from modifications in the liquid structure adjacent to surfaces. The presence of a surface induces a local ordering of the solvent and/or solute molecules. Two surfaces separated by less than the correlation length of this ordering probe this local structure as oscillatory structural forces. Short-range structural forces arise from surface-induced molecular ordering in the adjacent liquid layer and are termed *solvation forces* or, in water, *hydration forces*. Long-range structural forces are encountered, *e.g.*, in aqueous polyelectrolyte solutions of moderate concentration. The volume enclosed by the solvated polymer coils plus their counter ion atmosphere can be a significant fraction of the total solution volume, resulting into local ordering of the coils.

Finally, we mention forces which arise from liquid flowing (*capillary forces* and *viscous forces* of confined liquid) and contact forces (*adhesion, elastic,* and *friction forces*). For a review on surface forces the reader is referred to, *e.g.*, the book by Israelachvili [6].

Measuring surface forces accurately is an experimental challenge. In the past information on surface interactions was for the most part gathered indirectly, *e.g.*, by measurements of the stability of colloidal dispersions and soap films, aggregation kinetics and diffraction studies of order in liquid suspensions. Nowadays, various techniques are available to measure surface forces directly and accurately, the most well-known probable being the *surface force apparatus (SFA)* and *colloidal probe atomic force microscopy (colloidal probe AFM)*. The latter technique is used in the work described in this thesis. Direct force measurement techniques have provided and are still providing increasing insight into the great variety of surface forces that exist, and have made the subject a hot-topic in physicochemical research.

Aim of the project

The aim of the project at the basis of this thesis was twofold. In the first place it comprised implementation of colloidal probe AFM as an operational surface force measurement technique in our laboratory. The AFM was already available. This part of the work consisted of constructing a set-up for glueing particles on AFM tips,

choosing and testing a suitable procedure for calibration of the AFM cantilever spring constants and evaluation of the accuracy of the force measurements by comparison with theory and measurements reported in literature. Secondly, the aim was to investigate the influence of functional surface groups on the adhesion of colloidal particles to macroscopic surfaces, and the interaction between polymer-covered surfaces using the colloidal probe AFM technique. Because of the importance of a better understanding of the factors which play a role in the production process of many of the products produced by Philips, the project was supported scientifically as well a financially by Philips Research Laboratories, Eindhoven, The Netherlands.

Outline of thesis

The remainder of this chapter contains a first introduction to the atomic force microscope and surface force measuring techniques. In chapter 2 the colloidal probe AFM technique is discussed in detail. In chapter 3 force measurements on the model system silica - silica are described, in order to verify the results obtained with the colloidal probe AFM technique. The use of the silica-silica system allows for comparison with previous work by others using the same or other techniques. In the same chapter the work on solid surfaces is extended to force measurements between gold surfaces and between gold and silica surfaces. In chapter 4 the interaction forces measured between a polymer-covered silica sphere and a polymer-covered silica plate at various pH values and electrolyte concentrations and for different polymer chain lengths are described. The polymer used is poly(ethylene oxide) (PEO). Finally, in chapter 5 forces between functionalised monolayers on both gold and silica surfaces are the subject of study. The interactions between COOH - functionalised layers, between NH₃ - layers and between NH₃ - and COOH - layers were studied as a function of ionisation state of the functional groups.

1.2 The atomic force microscope (AFM)

1.2.1 Introduction

The atomic force microscope (AFM) was invented in 1986 by Binnig, Quate and Gerber [7]. It was the first of the many variations on the scanning tunnelling microscope (STM) that exist today. All these scanning probe microscopes (SPMs) form a family of instruments that measure properties of surfaces. The importance of these novel microscopy techniques for atomic imaging was confirmed by the awarding of the Nobel prize, in 1986, to the inventors of the STM, G. Binnig and H. Rohrer [8]. The main feature of all scanning probe microscopes is that they map topography (or another surface property) by scanning a sharp probe over a surface. In the case of STM a voltage is applied between a sharp conducting tip (a thin metallic wire) and the surface. When the tip is brought within a distance of 1 nm from the surface, electrons from the tip 'tunnel' to the surface. The resulting current falls off exponentially with distance between tip and surface and this is exploited to map the topography of the surface. To apply this technique the sample has to be conductive. It is, however, possible to image thin organic films, biological macromolecules (DNA, proteins) and even complete cells on conductive substrates, but the imaging principle for these nonconductive materials is still unclear from a physical point of view [9].

In contrast to STM, an AFM instrument is capable of imaging both conducting and non-conducting samples. As a probe the AFM uses a tip that is mounted on the edge of a flexible cantilever. When a sample is scanned the interaction forces between the tip and the sample surface cause the cantilever to deflect. The deflection of the cantilever is monitored by an optical system in which a laser reflects from the back of the cantilever onto a split photodiode. The measuring principle of the AFM will be discussed in more detail in section 1.2.2.

In all scanning probe microscopes either the sample or the tip has to be moved with extreme precision to make high resolution imaging possible. This positioning is usually done by a piezoelectric scanner, a positioning device which is capable of moving the sample (or sometimes the tip) in x-, y- and z-directions with an accuracy even better than a tenth of a nanometre.

Since the invention of AFM a great number of other SPM techniques have been introduced and the scope of applications has grown enormously. For example, it is possible to measure the friction force between probe and sample by monitoring the lateral deflection (torsion) of the cantilever (friction or lateral force microscopy, FFM or LFM). Dielectric properties and surface potentials can be mapped by applying a voltage to the tip (electric force microscopy, EFM), magnetic forces by using a magnetic tip (magnetic force microscopy, MFM). In near-field scanning optical microscopy (NSOM), SPM is combined with optical techniques, in which the probe consists of a very thin (sub-wavelength sized) glass fibre. As light emanates from the tip, it illuminates an area of the sample approximately equal to the aperture size, which may be less than 25 nm. The collected light, reflected from the sample or emitted by fluorophores at the surface, originates from this small area. Thus, resolution in this optical technique is not limited by the wavelength, but by the size of the aperture.

Several dynamic non-contact and contact modes of operation, *i.e.*, modes in which the AFM cantilever/tip system is vibrating near or against the sample surface, have been

introduced to detect material properties such as elasticity and mass density on the nanometre scale. These material properties follow from shifts in the amplitude and/or phase of vibration. New SPM techniques and instruments in which SPM is combined with other techniques continue to develop. For an overview the reader is referred to refs. [9-14].

1.2.2 Measuring principle

The AFM, or any other SPM for that matter, is surprisingly simple in its concept. The microscope consists of a piezoelectric scanner, a probe, a laser, a detection system (see figure 1.1) and a computer.



Figure 1.1: Diagram of the most common AFM set-up.

The piezoelectric scanner may be considered the most important part of any SPM. The capability of this scanner to move the sample in three directions at sub-nanometre resolution provides the basis of the SPM technique. The other key feature of the AFM is the probe or tip. In contrast to radiation-based microscopy techniques, like scanning electron microscopy or classical optical microscopy, where the resolution of the images is determined by the wavelength of the radiation, in AFM the resolution is determined mainly by the size and geometry of the tip. The standard AFM tip, made from silicon nitride, has a pyramidal shape, about 5 μ m at the basis and with a tip apex radius of curvature in the order of 10 nm. In an AFM image the size and shape of the

tip may be reflected, especially when imaging very small features or relatively large height differences. To improve the resolution sharper tips ("high aspect ratio tips") may be used. These are made, for example, by sharpening of standard tips by oxidation or by growing thin filaments on standard tips by means of focused-ion-beam deposition. Carbon nanotubes [15], consisting of fullerenes of macroscopic length in one direction, seem to have ideal properties to be used as AFM tip: these nanotubes are only a few nanometres thick, yet they can be several microns long. They are very strong and will even survive a crash into the sample surface.

The tip is mounted at the end of a cantilever which is coated on the back with a reflective layer. Various cantilever types, each having different spring constants, can be used. The most commonly used cantilevers have a V-shape, making them less prone to lateral twisting and rolling as the tip jumps into and out of contact to the surface. Although the probe is one of the most important components of an AFM, it is, together with the cantilever on which it is mounted, typically a disposable item.

In the basic mode of operation of the AFM, the so-called *contact mode*, the cantilever is deflected upward and it exerts a spring force to the sample surface. The force can be as low as 10^{-9} Newtons, which is in the range of interatomic forces, which explains the name: atomic force microscopy. During imaging the deflection, and thus the force on the cantilever, can be kept at a constant value by adjusting the z-position of the piezo element. This means that when the tip encounters higher features on the surface the piezo moves the sample downwards, and when the tip is scanning lower features the piezo element moves the sample upwards. The feedback on and the movement of the piezo is controlled by a computer.

When the feedback is kept high the sample is scanned under constant force and the *z*-movement of the piezo reflects the topography of the sample. This is more or less the standard way of imaging in the AFM and is commonly know as *constant force* or *height mode*.

The feedback can also be kept very low. Then the z-position or the height of the piezo is hardly altered during scanning. Now the cantilever will change its deflection, depending on the local height of the sample. In this *deflection mode* the deflection of the cantilever is plotted as a function of x, y position on the surface rather than the z-movement of the piezo element.

For most applications the force exerted on the sample can be kept low enough to avoid deformation or damage of the surface. For imaging of soft (organic) surfaces or molecular layers that are not firmly attached to the surface, special modes of operation have been developed, for example the *tapping mode*. In the tapping mode the contact

time between the tip and the sample is strongly reduced. For imaging in air a stiff cantilever is forced to oscillate vertically at a certain distance from the sample surface while scanning laterally. When the tip-sample distance decreases, the frequency and the amplitude of oscillation changes. The feedback system then lowers the position of the sample so that the cantilever regains its original amplitude of oscillation. Tapping mode in liquid operates in a slightly different way and a much softer cantilever is used. A description of the technique in air as well as in liquid is given in ref. [16]. In the tapping mode forces acting laterally to the sample are virtually eliminated and the frequency of oscillation is so high that the collisions between tip and sample are completely elastic. Very soft and delicate objects, such as surface micelles, have been studied in this way.

1.2.3 The AFM as a surface force apparatus

The atomic force microscope is indeed a microscope, because it magnifies surfaces so that we can look at them and study them. The basis of the technique relies on the measurement of and accurate control over the smallest of forces. Therefore, the apparatus might just as well have been called the *imaging surface force apparatus*. Today, the AFM is more and more referred to as the *scanning force microscope* (*SFM*).

From the start much attention has been paid to the forces acting between the AFM tip and the sample surface. Minimising these forces was necessary to improve the quality of the images and to prevent deformation of the samples. A considerable amount of effort was put into the investigation of the role of the forces during image scanning [17]. It is not surprising that at some point the forces themselves became a main subject of study. In the early 1990s several studies were published [18-20] in which the force between the tip and a flat surface is measured as a function of their separation. Unfortunately, because the geometry of the tip was not known, quantitative comparison with theory was not possible. An important step to overcome this problem was made by Ducker and co-workers [21, 22]. They were the first to attach a silica sphere at the end of an AFM cantilever and to measure forces between this silica particle and a silica plate. The use of a colloidal sphere, of which both the surface chemistry and the geometry are know, is what makes it possible to compare experiment and theory. An additional advantage is that the forces between such a colloidal probe (diameter of the order of several μ m) and a flat surface are much larger than between the AFM tip and a flat surface, and therefore can be measured much more accurately. Due to this development, nowadays AFM is not only a versatile imaging technique, but also has grown into an important surface force technique.

1.3 Surface force measurement techniques

1.3.1 Introduction

Over the years several techniques have been developed to measure directly interaction forces between surfaces as a function of their separation distance. Back in 1954 Derjaguin and Abricossova [23] already measured the Van der Waals attraction between a glass sphere and a flat glass plate in vacuum. They used a force-feedback technique in which the separation between the glass surfaces was determined optically and the interaction force was measured using an electrobalance. Using this set-up accurate measurements were made in the separation range 100 - 700 nm. The results were reasonably in accordance with predictions of the Lifshitz theory of Van der Waals forces.

Around the same time Overbeek and Sparnaay [24, 25] measured the Van der Waals interaction between parallel quartz glass plates in air using a spring balance. The surfaces were displaced using an air flow. The separation was determined optically by the colour of interference fringes, or below 100 nm by the intensity of the reflected light.

In 1969 Tabor and Winterton [26] introduced a force-balance in which two surfaces were placed in a crossed-cylinder geometry. Because of their molecular smoothness, transparency and flexibility, thin sheets of cleaved mica were used as the surface material. One of the surfaces was mounted on a piezo-electric device and the other on a flexible leaf-spring of known spring constant. The separation between the surfaces was determined optically, using an interferometric technique. The deflection of the leaf spring (and thus the force) at a particular separation was simply derived from the difference between the distance travelled by the piezo element and the actual displacement of the surfaces relative to each other. The apparatus of Tabor and Winterton has been further developed by Israelachvili and co-workers [27, 28] into the now well-know and widely used *surface force apparatus (SFA)*.

In the SFA the determination of both *force* and *distance* between the surfaces depends on the interferometric technique. This limits the application of surface force measurements in the SFA to transparent and/or reflective surface materials. Therefore, the search for alternative techniques continued. However, when the optical method is dismissed not only another way of determining the distance between the surfaces is needed but also a force sensor of some sort.

The development of the *bimorph force sensor* [29, 30] offered a new possibility. Bimorphs are essentially nothing more than two layers of piezoelectric material mounted on top of each other in reverse polarity. They can be used as leaf springs and under most conditions there is a linear relationship between the degree of deflection and their voltage output. Bimorphs were already used in the SFA as an addition to the interferometric measurement of the separation. The bimorph force sensor is used in a relatively new apparatus, the so-called *MASIF (Measurement and Analysis of Surface Interaction and Forces)*. In this device one surface is mounted on a piezoelectric tube and the other on a bimorph force sensor. The separation between the surfaces follows from the piezo travel and the deflection of the bimorph (from the latter also the interaction force is obtained). The surfaces are assumed to be in contact (zero separation) when the change in deflection equals the piezo travel.

In the next subsections the SFA and MASIF techniques as well as the colloidal probe AFM technique will be discussed in somewhat more detail and a comparison will be made between these techniques.

Other techniques that have been developed to measure surfaces forces, are, for example, the thin film balance [31, 32] to measure forces between liquid interfaces, the osmotic stress method [33] to measure forces between liquid-crystalline phases, and total internal reflection microscopy (TIRM) [34] in which the repulsive force between a particle immersed in a liquid and a transparent surface beneath it is determined from their average separation.

1.3.2 The Israelachvili Surface Force Apparatus (SFA)

In the surface force apparatus (SFA), schematically shown in figure 1.2, two molecularly smooth surfaces (usually muscovite mica) immersed in a liquid are brought towards each other and during this movement the force is recorded. The two surfaces are placed in a crossed-cylinder geometry, which is equivalent to a sphere-flat geometry [35]. The radii of curvature of the cylinders are roughly 1 cm. This leads to interacting areas in the order of several hundreds of μm^2 , assuming that the force acts over a distance in the order of 10 nm. The surfaces are moved towards or away from each other by a micrometer shaft (coarse positioning, upper rod in figure 1.2), a micrometer via a double cantilever spring (down to nm positioning, lower rod), and a piezoelectric tube (finest positioning, about 0.1 nm). The piezoelectric tube contracts or expands by applying a voltage across the tube.



Figure 1.2: Surface force apparatus (SFA) schematically. (Redrawn from J.N. Israelachvili, Intermolecular and Surface Forces, Academic Press, London, 1992)

The distance between the surfaces is determined by means of interferometry. To this end the mica sheets are coated on the backside with a semi-transparent silver layer. Light from a white light source is passed through the mica surfaces and via a microscope objective, which is directly mounted above the mica sheets, into a spectrometer. The distance between the surfaces is obtained from the fringes in the spectrogram, with an accuracy of about 0.1 nm. Furthermore, the local radius of curvature of the interacting surfaces can be determined from the shape of the interference fringes. Even the piezo can be calibrated using the interferometric technique because the exact distance between the surfaces is known.

The force is measured using a spring of which the spring stiffness can be adjusted during an experiment. The measurement of a force-distance curve is a stepwise process. In each step the piezo position is changed and the distance between the surfaces is determined. A difference in the distance over which the piezo has been moved and the displacement of one surface relative to the other is caused by a force acting between the surfaces. This difference is converted into the interaction force simply by multiplying it by the spring constant (Hooke's law).

An obvious limitation of the SFA is that the surfaces have to be transparent, atomically smooth over a relatively large area, and flexible so that they can be bent into a cylindrical shape. This puts severe restrictions on the number and diversity of systems that can be investigated. As a result most of the work with the SFA has been done on mica and on thin organic films deposited on mica, like protein adsorption layers [36], Langmuir-Blodgett films [37] or polymer films [38, 39]. Alternative materials to mica have also been introduced, for example silica [40, 41] or sapphire [42].

The development of the SFA is still going on. For example, modifications to the SFA allow for moving surfaces tangential relative to each other, which can be used to study shearing and friction forces [43-45].

1.3.3 The MASIF

The MASIF measures forces between a surface which is mounted on a piezoelectric tube and a surface which is mounted on a bimorph force sensor. See figure 1.3.



Figure 1.3: Scheme of the MASIF apparatus.

The surfaces are first brought into contact and then separated again. The piezoelectric tube moves the surfaces towards and away from each other. The force runs are done in a continuous way of approach and retract and during this operation the output of the

bimorph force sensor is recorded. In the MASIF usually a sensor (LVDT, linearly variable differential transformer) is mounted parallel to the piezo. This sensor monitors the expansion of the piezo, making it possible to correct for creep and hysteresis, which always play a role in piezoelectric devices.

As described before (see section 1.3.1) the separation of the surfaces is not directly measured, but deduced from the piezo position and deflection of the bimorph. Because there is no direct determination of the surface separation, it is not possible to determine the thickness of adsorbed layers.

The MASIF can measure forces between non-transparent surfaces. Furthermore, it allows for rapid force measurements permitting non-equilibrium and time-dependent measurements. Most work has been done with glass spheres, formed by heating a glass rod until a sphere forms on the end. The spheres typically have a diameter of 2.5 - 4 mm depending on the rod size used and the extent to which to sphere is allowed to grow. The order of magnitude of the interaction areas is $100 \ \mu m^2$ (for forces acting over *ca.* 10 nm).

1.3.4 Colloidal Probe AFM

In the colloidal probe technique a spherical particle is glued to an AFM cantilever. The cantilever is placed in the AFM and the force between this particle and a surface is determined as a function of distance (see figure 1.4). For particles with diameters in the range of 2 - 10 μ m, the interaction areas are in the order of 0.1 μ m², assuming that the force acts over a distance of *ca*. 10 nm. The surface is moved towards and away from the particle by the piezoelectric tube, like in the MASIF in a continuous motion. During each cycle the surfaces are brought into contact.

The raw interaction data obtained by the AFM consist of the measured deflection of the cantilever as a function of the z-position of the piezo. The deflection of the cantilever and thus the force between the surfaces is monitored by recording the position of the laser spot, which reflects from the back of the cantilever, on the photodiode. The photodiode output (in Volts) is converted into the deflection of the cantilever in the z-direction as follows. In the raw data a region is found where the photodiode signal is a linear function of the piezo position. In this region the particle on the cantilever is in contact with the sample surface on the piezo. Changes in the displacement of the sample are then equal to the changes in the deflection of the cantilever. The slope of the photodiode output *vs.* piezo position in this so-called *constant compliance* region gives the conversion factor to obtain the deflection in nanometres. Subsequently, for each point of the raw data curve, the interaction force can be calculated using Hooke's law, provided that the cantilever spring constant is



known. Zero of force (and deflection) is taken from the region where the particle and surface are far apart and the photodiode output has a constant value.

Figure 1.4: Colloidal probe measurement in the AFM.

The distance between the particle surface and the flat surface is not measured directly, but obtained in a way similar to that applied in the MASIF technique. The surfaces are assumed to be in contact in the constant compliance region; the start of this region when the surfaces are approaching each other is taken as the point of zero separation. Like in the MASIF, it is not possible to determine the thickness of adsorbed layers. Adsorbed layers which do not compress are virtually undetected and then the point of zero separation is, in error, taken to be the point where the adsorbed layers are in contact.

Because we need to include the zero point of force, where the surfaces are far apart, and because the software only allows to take a limited number of data points over the whole piezo range sometimes a poor resolution is obtained in the force curve. Furthermore, the surfaces are pressed together and separated again in a continuous cycle which makes it almost impossible to get a first-contact curve. However, with the development of this new technique continuing we may soon expect AFM-like instruments which are exclusively designed for the measurement of surface forces. These new surface force microscopes will surely overcome some of the disadvantages of today's commercial AFMs.

1.3.5 Comparison

The MASIF bears much resemblance to the AFM but also to the SFA. In the MASIF the SFA's optical interferometric technique has been dropped to be able to measure on non-transparent surfaces. With this, however, the direct determination of the surface separation is also lost. In the MASIF, like in the AFM, any sort of surface can be used, though the interacting areas are much larger than in the AFM. As in the SFA this leads to a better force resolution, but on the other hand the surfaces need to be smooth on a large scale and are more prone to contamination, like in the SFA.

Force measurements in the AFM are relatively easy to perform, yet gluing a particle or calibrating a cantilever can sometimes be a daunting task. Furthermore, in the AFM and in the MASIF measurements can be performed with speeds much higher than in the SFA, which makes it possible to measure relaxation effects or to measure at speeds corresponding to the rate of Brownian collisions between dispersed colloidal particles. On the other hand, the SFA has the advantage that it is possible to measure (equilibrium) properties of adsorption layers, *e.g.*, their thickness.

Table 1.1 lists the main differences between the force measurement techniques SFA, MASIF and Colloidal Probe AFM. When comparing these techniques it becomes evident that they all have their specific qualities and shortcomings and none of these machines is perfect or ideal for all systems.

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Table 1.1: Comparison of surface force measurement techniques. In all three techniques one of the surfaces is mounted on a piezoelectric device and the other on a leaf spring or a comparable element which deflects as a result of the force between the surfaces.

	SFA	MASIF	colloidal probe AFM
data directly obtained data deduced	surface separation as a function of piezo position deflection of leaf spring and from this the interaction force	deflection of the bimorph as a function of piezo position surface separation; zero of separation from constant compliance region	deflection of the cantilever spring as a function of piezo position see MASIF
time scale of measurements	very slow (< 0.01 Hz), step-wise approach and retract	see AFM; problems might arise during long-time experiments (>30 min) due to discharge of the bimorph	very fast (up to 100 Hz), making measurement possible of relaxation effects and <i>Brownian-like</i> collision rates
application limited to	transparent surfaces, which are atomically flat over areas of several hundreds of μm^2 and can be bent into a cylindrical shape	spherical surfaces flat over areas of about 100 μm ²	any surface (atomically flat only over areas of about 0.1 μ m ²) and any spherical particle of diameter in the range of 2 - 20 μ m
radius of curvature	determined from interferometry	determined by SEM	from particle size determined by SEM
remarks	large areas and thus prone to contamination	see SFA	smaller interacting areas meaning lower F/R resolution than in the SFA or MASIF.
	measurements are not easy to perform		cantilever calibration is difficult and a lot of work
		For soft surfaces and adsorption layers the absolute zero of separation is not determinable	see MASIF

1.4 Review of AFM force measurements

The first force measurements with the AFM were performed primarily to improve the quality of the images; lowering the force leads to a better image resolution and reduces the change of damaging the sample. Weisenhorn and co-workers [17] demonstrated the use of the AFM as a force apparatus by measuring the absolute force applied by a standard silicon nitride tip on a mica surface as a function of the z-position of the piezo. Based on their force versus distance curves they proposed a procedure to set the lowest possible image force: this was found to be *ca.* 100 nN in air and as low as 1 nN in water. In air on retraction a large adhesion force was observed, caused by the presence of a thin layer of water on the sample (and the tip).

This large adhesion in air has been used by Mate [46] to measure thicknesses of adsorbed water layers. He simply recorded the distance between the start of the adsorbed layer and the position where the tip touches the surface.

Weisenhorn [17] attributed the much smaller attractive forces between tip and mica surface in water to Van der Waals interactions. Later, force measurements by Weisenhorn [47] confirmed Hartmann's [48] calculations that attractive Van der Waals forces can be substantially reduced by operating in other solvents, for example ethanol.

Were the first force studies driven by the need to improve imaging with the AFM, soon the ability of the microscope to measure forces was applied by scientists who were interested in surface forces as such: for example, by Ducker [19, 49] who used changes in the resonance frequency of the cantilever to measure Van der Waals interactions and capillary forces, and by Burnham [18], who measured attraction and adhesion between a tungsten AFM-tip and different types of surfaces (mica, graphite, polytetrafluoroethylene, aluminium and Langmuir-Blodgett monolayer films of stearic acid) in dry nitrogen atmosphere. Electrostatic interactions between various tips and mica or glass surfaces in aqueous solution were investigated by Butt [50] as a function of pH and ionic strength of the solution.

The next step was made by Ducker and coworkers [22] who was the first to glue a spherical (silica) particle to the cantilever, thus eliminating the uncertainties in the tip size and geometry and making comparison with theory possible. They studied the interactions between a silica sphere and a silica plate in aqueous solutions at different pH values and salt concentrations. The results at separations greater than 3 nm, the electrostatic repulsion, agreed well with the force predicted by DLVO theory.

Since then a great number of systems have been investigated using colloidal probe AFM, using spheres of silica [21, 22, 51], gold [52, 53], zircon [54], iron oxide [55],

zinc sulphide [56, 57], and other materials. Also polymer-covered spheres have been used to investigate bridging between surfaces [58-61]. See also this thesis, chapter 4.

Using colloidal probes it is also possible to investigate true symmetrical systems, by measuring the interaction between two identical spheres [57, 62]. Colloidal probe AFM is even used to measure forces between silica spheres and air bubbles [63, 64].

Related to colloidal probe AFM is *chemical imaging AFM*. Here instead of a using a sphere with a certain chemistry the tip is modified with, for example, a functionalised monolayer [65-67] or a layer of individual ligand-receptor pairs [68, 69]. Scanning with such a modified tip will give an image of the surface where the chemical functionality or biological specificity can be seen on the surfaces. This is comparable to, for example, friction force microscopy. In chemical force imaging often in each point of the image a force curve is measured. However, since the tip size and geometry are not known and the resolution of the force curves is low, the technique only allows to determine the adhesion force at each point relative to that at other positions on the surface. Therefore, it should be regarded as an extension to AFM imaging and not so much as a way to accurately or quantitatively measure adhesion forces.

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Colloidal Probe AFM - Experimental Methodology

2.1 Introduction

In this chapter the experimental procedures for measuring surface forces using an atomic force microscope (AFM) are described. In the following sections we discuss successively the preparation of the colloidal probe, the calibration of the cantilever, the force measurements and the conversion of the collected data into force-distance curves.

The force measurements described in this thesis were done using a DI (Digital Instruments Inc., Santa Barbara CA, USA) NanoScope III atomic force microscope equipped with a standard fluid cell and a piezo scanner "E" (x, y range 12.5 μ m x 12.5 μ m).

2.2 Attaching particles to the AFM cantilever

Attaching a particle to a cantilever is in principle very simple: a sharp wire is used to put glue on a standard cantilever. Subsequently, a single particle is picked up with another sharp wire and placed on the glue. Generally, these actions are performed under an optical microscope and using a micromanipulator.

The set-up used in this work to glue particles is schematically shown in figure 2.1. It comprises a metallurgical optical microscope, *i.e.*, a microscope which illuminates the sample through the lens, a micromanipulator and a heating stage. The micromanipulator was built by Philips Research Laboratories (Eindhoven, The Netherlands). It essentially consists of two three-way translation stages allowing two objects to be moved in three directions independently from each other. The movements can be made with a precision of about 1 μ m.

In most of the experiments described in this thesis silica spheres were used as colloidal probes. The diameter of these particles is $6.0 \mu m$, as determined by electron microscopy. To determine the size of other particles used in this study, such as

tungsten particles, we have calibrated the monitor which is connected to the optical microscope.



Figure 2.1: The set-up used to glue particles to the end of AFM cantilevers.

The colloidal particles were glued to the cantilever using an epoxy resin, Epikote 1004 (Shell, Amsterdam, The Netherlands). This epoxy resin melts at about 100° C and is highly insoluble in water. The colloidal particles were glued to standard (V-shaped) contact-mode cantilevers with integrated tip (Digital Instruments Inc., Santa Barbara CA, USA). All the experiments in this thesis were done with "wide-legged" cantilevers, 200 μ m or 100 μ m long (see also section 2.3.1).

To glue a particle to a cantilever first a tungsten wire (0.25 mm diameter) is etched by immersing one end in 1 M KOH and applying an a.c. voltage of about 40 volts between the wire and a platinum electrode placed in the solution. The tungsten wire is etched until the end is only about 1 μ m thick. After etching the wire is rinsed in ethanol, dried in a stream of nitrogen and clamped in the micromanipulator.

Some epoxy resin dust is sprinkled onto a glass slide which is placed on the heating stage under the microscope. The heating stage is kept at a temperature of about 100° C, sufficient to melt the glue particles. Using the micromanipulator the sharp wire is dipped into one of the small glue droplets on the glass slide and some glue will attach to it. The amount of glue on the wire can be reduced by letting it touch a clean

part of the glass slide. This is repeated until only a tiny amount of glue is left on the wire. Now, the cantilever is placed on the heating stage and is rubbed with the glue-loaded wire tip exactly on the spot where the particle will be placed. In this way some of the glue on the wire is transferred to the cantilever. Even if there is no glue visible on the cantilever under the microscope, there is probably enough present to hold a particle.

The next step is to bring a small number of colloidal probe particles onto a clean glass slide under the microscope. The micromanipulator provided with a clean tungsten wire, sharpened as described before, is used to bring a single particle to the cantilever. Generally, the particle is readily picked up when touched as a result of capillary adhesion between the thin water films on the wire and the particle, which are always present under ambient conditions. Next, the particle is carefully manoeuvred onto the glue on the cantilever where is sticks. Finally, the cantilever is removed from the heating stage, after which the glue hardens. Some representative pictures of the results are shown in figure 2.2.



Figure 2.2: Scanning electron micrographs of silica particles glued to AFM cantilevers. The left picture shows a 6 micron silica particle glued in the standard way, the right picture shows a 1.5 micron particle glued at the top of the cantilever tip.

2.3 Determination of the cantilever spring constant

2.3.1 Introduction

In AFM force measurements forces are usually calculated using Hooke's law:

$$F = -kz \tag{2.1}$$

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where F is the force, k the cantilever spring constant, and z the deflection of the cantilever. The cantilevers used throughout this work were obtained from Digital Instruments (Santa Barbara CA, USA). The cantilevers are mounted on a substrate or chip. Several hundreds of these substrates are mounted in a single wafer. Four types of cantilevers are provided on one substrate (see figure 2.3): 100 μ m long *wide-legged*, 100 μ m long *narrow-legged*, 200 μ m long *wide-legged*, and 200 μ m long *narrow-legged*, 200 μ m long *wide-legged*, and 200 μ m long *narrow-legged*. Digital Instruments specifies the spring constants of the various cantilever types, but the values provided indicate only the order of magnitude. Slight variations in, for example, the thickness of the reflective gold coating on a cantilever wafer may result into large differences (differences of a factor 10 or 20 are not uncommon) in the spring constants of cantilevers of the same type on that wafer. For AFM imaging it suffices to know only the order of magnitude of the spring constant. However, for accurate force measurements and comparison with theory it is necessary to precisely determine the spring constant of each individual cantilever.



Figure 2.3: Schematic depiction of two of the 4 cantilevers on one substrate. The cantilevers shown are 100 μ m and 200 μ m wide-legged cantilevers. The two thin-legged cantilevers are mounted at the other end of the substrate.

Various methods to measure the cantilever spring constant have been proposed. The most obvious way is to apply a known force to the end of the cantilever and measure the resulting deflection. This is done, for example, in a set-up as described by Butt *et al.* [1] in which a small pendulum is placed against a vertically mounted cantilever. By slightly tilting the set-up an adjustable force is applied to the cantilever. A laser is used to determine its resulting deflection. Senden and Ducker [2] proposed a simple method which employs the AFM head piece, *i.e.*, the cantilever holder and the optical detection system for measuring cantilever deflection. In this method a tungsten sphere (10-50 μ m in diameter) of known mass is attached to the end of the cantilever (and the resulting deflection of the cantilever is measured. After placing the cantilever (and the AFM head) upside down, the cantilever deflection is measured again. The difference between the two measurements is twice the deflection due to gravity, from which the spring constant can be determined.

Torii *et al.* [3] described a method in which a large-scale cantilever is used to apply an increasing force to the AFM cantilever. The deflections of both cantilevers are measured simultaneously using heterodyne interferometry. Since the spring constant of the large-scale cantilever is calibrated accurately, the spring constant of the AFM cantilever can be calculated from the force curve. Smith and Howard [4] have built a precision low-force balance to measure the spring constant.

Apart from these static methods, several methods have been described in which the spring constant is determined from the resonance frequency of the unloaded cantilever [5] or the shift in the resonance frequency of the cantilever when loaded with particles of known mass [6]. The latter method, proposed by Jason Cleveland of the University of California, has been used in this work for calibration of the cantilever spring constant, and is henceforth referred to as *the Cleveland method*. Just measuring the resonance frequency of the unloaded cantilever was used for a quick evaluation of the spring constant in preliminary force measurements. Therefore, these two methods are described in more detail in sections 2.3.2 and 2.3.3.

Finally, a number of investigators [7 - 9] have tried to calculate the spring constant of the cantilever from its shape, dimensions and material properties. To this end, models were introduced to approximate the V-shaped cantilever. The most commonly used is the so-called *two-beam approximation*, in which the cantilever is described by two rectangular beams in parallel. This leads to the following expression for the spring constant k [9]:

$$k = \left(\frac{t}{l}\right)^3 \frac{Ew}{4} \tag{2.2}$$

in which E is the elastic modulus, *i.e.*, the Young's modulus of the bulk material, and t, w, and l are the thickness, width and length of the cantilever beams, respectively. The width and length of the cantilever beams can be determined quite accurately and the variation in these values for the same type of cantilevers on one wafer is very small. However, cantilevers are often very thin and, as stated before, there may be significant differences in the thickness between cantilevers on one wafer. Since in equation 2.2 the thickness is cubed, this may lead to large deviations from the actual spring constant values. To determine the spring constant would now involve measuring the thickness of the individual cantilevers. Even if this were a simple task the spring constant might still be questionable because the applicability of the calculated value also relies on the accurate knowledge of the elastic modulus. This modulus varies due to (local) variations in the stoichiometry of the silicon nitride and that of the gold coating, which are unavoidable in microfabrication techniques.

To avoid the use of a (too simple) model for the cantilever shape, Sader and White [9] performed a finite element analysis of the static deflection of V-shape cantilevers and presented exact numerical results for the spring constant for a variety of cantilever dimensions. However, also in this approach the results directly depend on accurate values for the thickness and elastic modulus of the cantilever, which are not easily accessible. This restricts the applicability of any model calculation of the spring constant. In practice, *measurement* of the spring constant of the individual cantilever is still the best option to get quantitatively reliable results from force measurements.

2.3.2 The Cleveland method

In this work the *Cleveland method* [6] was used for calibrating the cantilevers. In this method, particles of known size and density are attached to the free end of the cantilever and the spring constant k is determined from the resulting shift of the cantilever's resonance frequency. Using this method it is not necessary to know the mass of the cantilever itself.

The resonance frequency v_0 of the unloaded cantilever is given by:

$$v_0 = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$
(2.3)

The cantilever is here approximated as a spring with spring constant k and an effective mass m. When a mass M is added to the end of the cantilever this becomes:
$$v = \frac{1}{2\pi} \sqrt{\frac{k}{m+M}}$$
(2.4)

Rearranging this equation gives:

$$M = \frac{k}{\left(2\pi\nu\right)^2} - m \tag{2.5}$$

Thus, measuring the resonance frequencies of the cantilever for various attached masses and plotting M as a function of $(2\pi v)^{-2}$ should give a line with a slope equal to the spring constant. If desired, the effective cantilever mass follows from the intercept of this plot for $1/v^2 = 0$.

The resonance frequency of the cantilever can be easily determined making use of the NanoScope software. First the resonance frequency v_0 of the unloaded cantilever is determined. After this a particle of known mass is attached to the cantilever, and the resonance frequency is again measured. Attaching the end mass is done in much the same way as with the colloidal probes, only this time no glue is used (in air the particles stick due to capillary adhesion). As end masses we used tungsten spheres with diameters in the range 10 - 30 μ m (see figure 2.4). The masses of the spheres were calculated from the sphere radii and the density of tungsten (19.3·10³ kg/m³).



Figure 2.4: Scanning electron micrograph of the tungsten particles used in calibrating the cantilevers.

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In principle, measuring the resonance frequencies of the unloaded cantilever and the loaded cantilever for just one value of M would suffice to calculate k from equations 2.3 and 2.4. However, in practice more measurements are needed to reduce the effect of experimental errors, in particular those related to determining the precise size of the tungsten particles. An example of a spring constant calibration plot is given in figure 2.5.



Figure 2.5: Typical cantilever calibration plot for a standard 200 µm wide-legged DI cantilever. Spring constant 0.108 N/m; correlation coefficient 0.98.

2.3.3 Estimation of the spring constant

For cantilevers differing in thickness but otherwise identical, the spring constants are proportional to the cube of their unloaded resonance frequencies. This is expressed in the following equation [6]:

$$k = 2\pi^3 l^3 w \rho^{3/2} E^{-1/2} (v_0)^3$$
(2.6)

with ρ the (effective) density of the cantilever material, and v_0 the resonance frequency of the unloaded cantilever. The other parameters were defined below equation 2.2.

In figure 2.6 the spring constants of a number of cantilevers originating from the same wafer are plotted against their cubed unloaded resonance frequencies. A linear relation is found, indicating that variations in the dimensions (width, length) and elastic properties of these cantilevers are relatively small. This relation provides a first estimate for the spring constant of a cantilever on the basis of its unloaded resonance frequency.



Figure 2.6: Spring constants for a number of cantilevers from one wafer plotted against their cubed resonance frequencies. The cantilevers used were DI standard contact-mode cantilevers, 200 μ m long wide-legged. Linear regression: $k = V_0^3 \cdot 1.13 \cdot 10^{-5}$; correlation coefficient 0.988. On the lower horizontal scale the cubed resonance frequency is replaced by the corresponding resonance frequency which facilitates the possibility to directly estimate the spring constant from the graph.

The data points given in figure 2.6 were determined using the Cleveland method, but, of course, such a master curve can be generated using any other method for measuring the spring constant. Because it is likely that the variation in the elastic modulus of the material between different wafers is much larger than within one wafer, such a graph should be constructed for each particular wafer and only be used to estimate the spring constants of the cantilevers on that wafer.

Graphs like the one in figure 2.6 were used throughout this work to estimate the spring constants of the cantilevers used in tentative force measurements. Cantilevers used for

final measurements were always calibrated using the Cleveland method, as described in section 2.3.2.

2.4 Force measurements

During force measurements in the AFM, the tip (with or without a colloidal probe) and a flat surface are continuously brought into contact and separated again. The piezo element moves only in the z-direction; the x and y positions are fixed.

Since the flat surface is mounted on the piezo element, the flat surface is brought towards the cantilever rather than the cantilever towards the surface. In our experiments typically a scan rate of 1 Hz was used, for a z range of about 1 μ m.



Figure 2.7: A typical force graph in which the deflection of the cantilever is plotted against the piezo position. On the right, the position of the colloidal probe and the flat surface on the piezo are shown for several points of the curve, indicated by Roman numerals.

Forces acting between the surfaces will cause the cantilever to deflect. The deflection of the cantilever is monitored and plotted in a graph of deflection versus piezo movement. An example of such a graph is shown in figure 2.7. On the vertical axis the output of the photodiode is plotted and the horizontal axis gives the position of the piezo. The curve I-II-III gives the interaction on approach and the other (with the deep minimum) corresponds to the interaction upon retraction. At large distance (I) no force acts on the particle. When bringing the surface closer the particle feels an attraction or a repulsion which causes the cantilever to bend towards or away from the surface (II) (in figure 2.7 an attraction is depicted). When the particle and flat surface have come

into contact (provided the surfaces do not indent - or do not indent anymore), the particle movement complies to the movement of the piezo. This implies that when the piezo is moved upwards over a certain distance the probe is moved upwards over the same distance (III). Consequently, the measured deflection is linear with the piezo movement which shows up as a linear region in the force plot. This part of the curve is called the *constant compliance region*. At the end of this constant compliance region the piezo movement is reversed. If there is an adhesion between the surfaces a force is needed to separate them. This is illustrated in figure 2.7: on retraction the surfaces are in contact beyond the point where initial contact was made (IV). As the piezo is moved further downwards the surfaces are separated again. At larger distances the force between the tip or probe and the surface is again zero (V).

2.5 Construction of force versus distance curves

The *deflection versus piezo position* curve can be converted into a *force versus distance* curve, in which the force (in Newton) is plotted against the actual distance between the surfaces (see figure 2.8).

In order to do this, first the point of zero separation needs to be defined. This point of zero separation is derived from the constant compliance region in the raw data, where the surfaces are in contact. Therefore, the onset of the constant compliance regime is taken as the origin of the separation scale. It should be noted, however, that if there is an adsorption layer present at one or both of the surfaces, there is still a finite distance between the surfaces in the constant compliance region. In that case it is not possible to determine the absolute zero point of separation. Furthermore, if one or both of the surfaces is compressible, the onset of the constant compliance region does not coincide with the point of first contact.

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Figure 2.8: The raw data graph (A) is converted to a force distance graph (B). The dashed curve is the interaction on approach and the continuous curve is the interaction on retraction. In graph A the constant compliance region for the retraction is marked as well as the point were the curve deviates from this region. This point is taken to be the onset of the constant compliance region.

Once the point of zero separation is established, the separation is calculated from the distance travelled by the piezo and the change in cantilever deflection relative to the onset of the constant compliance region. The procedure is illustrated in figure 2.9. In this work the piezoelectric scanner was calibrated in the z direction by means of the method of Jaschke *et al.* [10]. In this method the piezo scanner is calibrated by using interference patterns from the AFM laser.



Figure 2.9: Calculation of the distance between the surfaces. In the picture to the left the surfaces are in contact, i.e. their separation d = 0 (constant compliance region). In the picture to the right the surfaces are no longer (or not yet) in contact. Relative to the left picture the piezo has travelled over a distance Δz_1 and the vertical deflection of the cantilever has moved over a distance Δz_2 . The distance between the surfaces is now $d = \Delta z_1 + \Delta z_2$. For our measurements the z-direction of the piezoelectric scanner was calibrated using the method of Jaschke et al. [10].

As described in section 1.2, the deflection of the cantilever is monitored by a split photodiode. The output in Volts of this photodiode is simply the difference between the voltage output of its top and bottom segments. To convert a change in voltage into a change of deflection in nm, again the constant compliance region is used. In this region the piezo movement and the movement of the probe are the same. Therefore, the *slope* (V/nm) of the constant compliance line provides the relation between the photodiode output (in Volts) and the cantilever deflection (in nanometres). This relation is also used in converting the vertical scale of figure 2.8a into a force scale. At large separations the voltage output of the photodiode is constant and this is taken as the zero of deflection and force. By subtracting this voltage-output from the actual voltage-output for each data point, converting the result into a deflection in nm (by dividing it by the slope of the constant compliance region), and multiplying this with the spring constant of the cantilever, we obtain the interaction force (in Newtons).

Usually, the force is displayed as a force divided by an effective radius R, in units of Newtons per metre. This quantity is related to the interaction energy per unit area U(D), between two flat surfaces at separation D, by

$$F(D)/R = 2\pi U(D) \tag{2.7}$$

This relation is know as the *Derjaguin approximation* [11] and is applicable when the range of interaction and the distance (D) between the surfaces is much less than the effective radius (R). For the interaction between two spheres the effective radius is defined as:

$$R = \left(\frac{R_1 R_2}{R_1 + R_2}\right) \tag{2.8}$$

From this equation it follows directly that when the radius of one sphere is much bigger than the other $(R_2 >> R_1)$, the effective radius equals R_1 .

$$R = R_{\rm I} \tag{2.9}$$

Obviously, this relation also holds for a sphere and a flat interface $(R_2 = \infty)$. Normalisation of the interaction force in this way, *i.e.*, presenting it as F/R, facilitates comparison of force measurements performed with colloidal probes of different sizes or in systems with different geometries.

2.6 References

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The Interaction between Solid Surfaces in Aqueous Electrolyte

Abstract: Silica-silica, gold-gold, and silica-gold interactions in aqueous electrolyte solutions have been studied using colloidal probe AFM. For all systems investigated the experimental force curves are dominated by electric double layer interactions. No indication whatsoever was found for an attractive Van der Waals component. For the silica - silica system the Van der Waals forces may be obscured due to a combination of solvent structural forces (hydration forces) and surface roughness effects. However, for gold-gold interactions the literature value of the Hamaker constant is so large that Van der Waals forces should definitely be noticeable in the force curves. The reason for this not being the case is as yet not clear. The effective electric potentials at the surfaces were determined by fitting the data to the DLVO theory or to the non-linear Poisson-Boltzmann equation (i.e., leaving out the Van der Waals interactions). The thus obtained potentials for silica as a function of pH and electrolyte concentration agree well with values reported in literature. Because of the lack of comparable literature data for gold, we determined the zeta-potentials of the gold surfaces at various pH values by streaming potential measurements. The correspondence between the zeta-potentials and the surface potentials from the gold-gold interaction curves was found to be quite reasonable. Results obtained for the silica-gold system were found to be in overall agreement with expectation. Above the iso-electric point of the gold surface $(pH \sim 4.5)$ both of the interacting surfaces are negatively charged resulting in electrostatic repulsion. At low pH the surfaces are oppositely charged and an attractive interaction is found. At pH 4, however, repulsion is observed where an attraction was expected; the force curve exhibits a small but distinct maximum at small separation indicating the onset of a change of repulsion into attraction upon approach. The results clearly illustrate that for dissimilar surfaces it is only possible to obtain reliable values for the surface potential if the electrostatic interactions are large over a long separation range, or if detailed knowledge on the charge regulation mechanisms of both surfaces is available.

3.1 Introduction

In this chapter force measurements on the model system silica - silica are used to verify the proper functioning of the colloidal probe AFM technique as implemented in our laboratory. To this end the interaction between silica surfaces in aqueous environment is determined as a function of electrolyte concentration and pH. The results are compared to literature data on similar systems as well as to theoretical predictions of the DLVO theory, named after Derjaguin and Landau [1] and Verwey and Overbeek [2]. Since we use this theory to fit our experimental force curves, the outline is described in the next section.

In addition to the measurements on the silica-silica system, force measurements have also been performed on gold-gold and silica-gold systems at various pH values. The results obtained for interactions between these bare surfaces also serve as "blanks" for the measurements described in chapter 4, concerning the interaction between polymercovered silica surfaces, and in chapter 5, which deals with the interaction between functionalised layers on gold and silica.

3.2 DLVO theory

The DLVO theory has been developed to describe the colloidal stability or instability of lyophobic sols. In this theory it is assumed that the interaction between colloidal particles in aqueous solution is determined by two types of forces: Van der Waals forces and electrostatic forces. Generally speaking, Van der Waals forces result from interactions between atomic or molecular dipoles. The dominant term in the Van der Waals interaction, the *London-Van der Waals interaction* or dispersion interaction, is due to the mutual effect of the (oscillating) electron clouds of two atoms or molecules on each other. Electrostatic interactions arise from charge separation across the particle/solution interface and overlap of the electric double layers of two particles.

3.2.1 Van der Waals forces

That an attractive force exists even between molecules which do not carry a charge or a permanent dipole becomes apparent when we realise that non-polar gasses, *e.g.* helium, can undergo a phase transition to the liquid state. The helium atom has no dipole when averaged over time. However, at any particular instant the electron density is not symmetrical around the atom nucleus. Therefore, the atom has a time-dependent dipole, fluctuating with a high frequency. When two atoms approach, their oscillating dipoles will start to influence each other, resulting in a net attraction. The magnitude of this attraction depends on the properties of the atoms involved or, more specifically, on their polarisability, *i.e.*, the ease in which their electron distributions can be relocated. Besides this London-Van der Waals interaction, Van der Waals forces include the interaction between a permanent dipole and an induced dipole (*Debye forces*), and a permanent dipole - permanent dipole interaction (*Keesom forces*). The interaction energies resulting from these forces are additive and are all proportional (in first approximation) to $1/D^6$, where D is the separation between the atoms or molecules. The total interaction energy due to Van der Waals forces can be written as:

$$u_A = -\beta D^{-6} \tag{3.1}$$

in which β is a proportionality constant accounting for the London, Debye and Keesom interactions ($\beta = \beta_L + \beta_D + \beta_K$). For a quantitative treatment the reader is referred to, for example, ref. [3].

Equation 3.1 applies to the interaction between two atoms or molecules. Extending it to describe a many-atom system is a complicated task. The so-called microscopic approach employs pairwise summation. In this method the interaction between each atom in the system with every other atom is simply summed, neglecting the fact that the internal state of each atom is changed by the presence of the other atoms. Yet, in many cases this provides a reasonable approximation.

In this way the total Van der Waals interaction between two colloidal particles is obtained by summation of the interaction of each atom of one of the particles with each atom of the other particle. The number of interacting atom pairs increases as R^6 , R being the radius of the particles. Since the Van der Waals force is inversely proportional to D^6 , for a constant ratio of R/D the Van der Waals interaction energy is approximately constant. Therefore, the Van der Waals interaction between two colloidal spheres at a distance equal to their diameter is of the same order of magnitude as the interaction between two atoms separated by one atom diameter.

For the interaction between a sphere and an infinite planar half-space at relatively short distance, the pairwise or *Hamaker* summation leads to the following equation [3]:

$$U_A(D) = -\frac{RA}{6D} \qquad (D \ll R) \qquad (3.2)$$

where R is de radius of the sphere, D the closest distance between the surfaces and A the so-called *Hamaker constant*. In the Hamaker constant the molecular properties of the materials under consideration are accounted for (the polarisability as expressed in the value of β , and the density). The Hamaker constant can be computed if these molecular properties are known. Alternatively, it can be derived from the (macroscopic) dielectric properties of the materials, or from experiment. If the Hamaker constant for interaction between two bodies of the same material *i* in vacuum is denoted as A_{ii} , the Hamaker constant between two bodies of different material (1 and 2) across a medium 3 $A_{12(3)}$ is approximately given by:

$$A_{12(3)} = (\sqrt{A_{11}} - \sqrt{A_{33}})(\sqrt{A_{22}} - \sqrt{A_{33}})$$
(3.3)

Clearly, Van der Waals interactions across a medium are considerably lower than in vacuum.

In the above it was tacitly assumed that the Hamaker constant is independent of separation distance D. In reality, the London-Van der Waals interaction falls off stronger than $1/D^6$. This is because for two interacting atoms at large separations, the electron distribution of the first atom has already changed by the time the information regarding its dipolar orientation, travelling at the finite speed of light, has reached the other atom. The interaction is then "retarded". Lifshitz [4, 5] took this retardation into account and calculated the London-Van der Waals interactions from quantum theory and statistical thermodynamics. It turns out that for two interacting atoms retardation must often be taken into account. In the retarded region the London-Van der Waals interaction between a sphere and a flat surface is described by an equation of the same shape as equation 3.2, but now the Hamaker "constant" is dependent on separation (A = A(D)).

3.2.2 Electrostatic interaction

The second type of interaction in the DLVO theory, the electrostatic interaction, results from the charge at the surfaces and the countercharge in solution.

For monovalent ions, the diffuse part of the double layer is adequately described by the *Gouy-Chapman (GC) theory* [6, 7]. However, as in the GC theory the ions in solution are regarded as point charges in a structureless continuum and the surface is assumed to be ideally smooth bearing a smeared out charge, deviations from this theory may be quite large near the surface. Many corrections to the GC theory have been proposed, the most well-known being undoubtedly the introduction of a Stern layer in the double layer model [8]. This extended model, the *Gouy-Chapman-Stern* (GCS) model accounts for the finite size of the ions (only near the surface) and for specific ion adsorption. For a treatment of the GCS model and for more refined double layer models the reader is referred to the extensive literature, of which an overview can be found in, *e.g.*, ref. [9].

Despite the shortcomings of the GC theory DLVO calculations and fits of experimental force-distance curves in this thesis are restricted to double layers of the Gouy-Chapman type. The reason for this is that the fit of the experimental data is not determined by the force curves at small distances. As will become clear, at small separations the boundary condition chosen to calculate the electrostatic interaction (constant surface potential or constant surface charge), surface roughness effects and interactions not accounted for in the DLVO theory play an important role. It is therefore rather pointless to fit the data to more rigorous double layer models.

In the Gouy-Chapman theory of the diffuse double layer the one-dimensional Poisson equation, which gives the relation of the electric potential ψ at a distance x from the surface to the space charge density ρ , is combined with the Boltzmann equation, which describes the concentrations n_i of ions of type i and their valency z_i in relation to their bulkconcentrations $n_{i,0}$, to give the *Poisson-Boltzmann equation*:

$$\frac{\mathrm{d}^2 \,\psi(x)}{\mathrm{d}\,x^2} = \frac{zen_0}{\varepsilon_o \varepsilon_r} \left(\mathrm{e}^{ze\psi(x)/kT} - \mathrm{e}^{-ze\psi(x)/kT} \right) \tag{3.4}$$

The linearisation of the Poisson-Boltzmann equation is called the *Debye-Hückel* approximation which applies when the electric energy in the exponents is smaller than the thermal energy (i.e., $ze\psi / kT < 1$, or $\psi < 25$ mV for T = 293 K and z = 1). Then, the equation can be reduced to:

$$\frac{d^2 \psi(x)}{dx^2} = \kappa^2 \cdot \psi(x)$$
(3.5)

In this κ^{-1} is the well-known *Debye length*, which depends on the solvent- and electrolyte properties and the temperature. Using the boundary conditions that at $x = \infty d\psi / dx = 0$ and at $x = 0 \psi = \psi_0$ equation 3.5 is solved into:

$$\Psi(x) = \Psi_0 e^{-\kappa x} \tag{3.6}$$

Since the one-dimensional Poisson equation has been used to obtain this result, equation 3.5 only applies to flat surfaces or relatively large colloidal particles (with radius $R >> \kappa^{-1}$).

When two surfaces of the same charge sign come close their double layers will overlap resulting in a higher concentration of counterions in the overlapping region. The difference in the (osmotic) pressure between the surfaces and the pressure in the bulk is driving the two surfaces apart. The excess osmotic pressure Π is calculated from the ionic concentrations at the midplane between the surfaces, $n_{i,midplane}$, and the ionic concentrations in the bulk $n_{i,0}$:

$$\Pi = kT \left(\sum_{i} n_{i, midplane} - \sum_{i} n_{i,0} \right)$$
(3.7)

For a symmetrical electrolyte, using the Boltzmann equation,

$$\Pi = kTn_0 \left[\left(e^{-2e\psi_{midplane} / kT} - 1 \right) + \left(e^{+2e\psi_{midplane} / kT} - 1 \right) \right]$$
(3.8)

which gives for not too high values of $\psi_{midplane}$:

$$\Pi = n_0 k T (ze \psi_{midplane} / kT)^2$$
(3.9)

The potential at the midplane is often taken to be the sum of the local potentials in the two single double layers (superposition approximation), *i.e.*, for a distance *D* between the surfaces with the same surface potential Ψ_0 , $\Psi_{midplane} = 2\Psi_0 \cdot e^{(-\kappa D/2)}$. This results into :

$$\Pi = 4 \frac{n_0 z^2 e^2}{kT} \psi_0^2 e^{-\kappa D}$$
(3.10)

or using the expression for the Debye length:

$$\Pi = 2\kappa^2 \varepsilon_o \varepsilon_r \psi_o^2 e^{-\kappa D}$$
(3.11)

The approximation of $\psi_{midplane}$ as being built up additively from the local potentials of the two single double layers is only correct for separation distances D larger than a

few times the Debye length κ^{-1} . For shorter distances the full Poisson-Boltzmann equation should be solved for two parallel plates at distance D. The only difference from the case of a single double layer is in the boundary conditions. Now, for similar surfaces, these are $\psi = \psi_0$ at x = 0 and x = D, and $d\psi/dx = 0$ halfway the plates, at x = D/2. For dissimilar surfaces with surface charge densities σ_1 and σ_2 one should use the boundary conditions

•
$$x = 0$$
 : $\psi = \psi_1$
 $x = D$: $\psi = \psi_2$
• $\sigma_1 + \sigma_2 = \varepsilon_0 \varepsilon_r \left[\left(\frac{\mathrm{d} \psi}{\mathrm{d} x} \right)_{x=D} - \left(\frac{\mathrm{d} \psi}{\mathrm{d} x} \right)_{x=0} \right]$
(3.12)

Integrating the pressure with respect to separation distance from infinity to D gives the electrostatic contribution to the interaction energy per unit area $U_e(D)$. The result of this integration depends on the chosen conditions. During the approach the charge on each of the surfaces may change under the influence of the interaction with the other surface. We consider two limiting cases. In the first one the charge on the surface stems from weakly ionisable surface groups and the approach is relatively slow, so that the surface groups are at any time during the approach in thermodynamic equilibrium with the solution. This implies that the surface charge changes in such a way that the surface potential ψ_0 is constant. In the second case the charge is fixed on the surface, as is the case, *e.g.* in clay minerals and for surfaces with strongly dissociating groups like sulfonate. Obviously, then the surface charge σ_0 is constant on approach. In many practical cases the interaction is such that neither the surface potential nor the surface charge is constant and the interaction curves are somewhere in between those for the two limiting cases.

Under the assumption of a (low) constant surface potential ψ_0 and using equation 3.11 one obtains for the symmetric case:

$$U_{e}(D) = 2\varepsilon_{a}\varepsilon_{r}\psi_{a}^{2}\kappa e^{-\kappa D}$$
 "constant potential" (3.13)

Using the Graham equation [10] to express equation 3.11 in terms of the surface charge density instead of Ψ_0 , and assuming that the σ_0 is constant, the integration of Π over distance results into:

$$U_e(D) = \frac{2\sigma_0^2 e^{-\kappa D}}{\varepsilon_r \varepsilon_0 \kappa} \qquad \text{``constant charge''} \qquad (3.14)$$

From the foregoing it is clear that equations 3.13 and 3.14 only apply for not too high (and equal) surface potentials ($\psi_0 < 25 \text{ mV}$), for flat double layers (*i.e.*, $\kappa^{-1} \ll R$) and interaction distances much smaller than R but larger than κ^{-1} .

3.2.3 Fit of experimental force-distance curves with the DLVO theory

According to the DLVO theory the total interaction energy between two charged surfaces in solution is the sum of the Van der Waals interaction energy and the electrostatic interaction energy $(U = U_A + U_e)$. In this thesis the electrostatic interaction has been calculated using the non-linear Poisson-Boltzmann equation (3.4) for two parallel surfaces and the complete expression for the disjoining osmotic pressure (3.8). In this way we are not restricted to the low-potential limit and separation distances larger than the Debye length, but it implies that numerical methods are necessary to perform the calculations. We used the numerical procedure described by Chan *et al.* [11]. Interaction curves were calculated for the boundary conditions of constant potential and constant charge. A non-retarded Hamaker constant has been used to calculate the Van der Waals interaction.

From the total interaction energy U(D) the normalised force F(D)/R acting between the surfaces was obtained using the Deryaguin approximation (equation 2.7). Theoretical force-distance curves have been fitted to the experimental ones with the surface potential ψ_0 at infinite separation as the only fitting parameter. It should be noted that although we use the term surface potential, the obtained values for ψ_0 are in fact diffuse double layer potentials and not potentials at the surface/solution interface. The corresponding σ_0 values represent the charge as compensated in the diffuse part of the double layer).

For asymmetric systems, *i.e.*, two interacting surfaces of different (chemical) nature, interaction curves were calculated using a computer program of Hillier [12]. It should be noted, however, that for asymmetric systems it is not possible to obtain unique values for the surface potentials from a fit with the theory. To get meaningful information it is required that for one of the surfaces the potential at infinite separation is known, for example, from earlier measurements on a symmetric system. Furthermore, for the case of unequal surfaces the boundary condition (constant charge or constant potential) is much more critical than for two surfaces at the same potential. In contrast to the situation of two similar surfaces, where the electrostatic interaction is always monotonically repulsive, for dissimilar surfaces it can be either attractive,

repulsive or nonmonotonic, depending on the degree of charge regulation on the interacting surfaces. For example, if the surface potentials at infinite separation are of the same sign but of different magnitude and one or both of the surfaces maintain(s) constant potential, then theory [13, 14] predicts that there will be a charge reversal on the surface of lower potential; the interaction will then change from repulsive to attractive. On the other hand, when the surfaces both maintain constant charge, there is repulsion at any separation distance. We will return to this issue in the discussion on the interaction between gold and silica surfaces (section 3.4.4).

3.3 Experimental

The silica spheres were a gift from Philips Research Laboratories (Eindhoven, The Netherlands). The diameter of the spheres as measured by electron microscopy is 6.0 μ m. Flat silica surfaces were obtained by oxidising silicon wafers to a depth of 100 nm. The roughness of the oxidised wafers, determined by AFM in imaging mode and defined as the root mean square (rms) of the height differences on the surface, was found to be about 2 nm over an area of 1 μ m².

The silica spheres were glued onto standard silicon nitride AFM cantilevers (Digital Instruments Inc., Santa Barbara, CA, USA) according to the procedure explained in section 2.2. The glue used for this purpose was Epikote 1004 (Shell, Amsterdam, The Netherlands). The cantilevers with silica spheres and the silica wafers were cleaned in a plasma cleaner (model pdc-32G, Harrick Scientific, New York, USA) just prior to the experiments. This cleaning resulted in hydrophilic silica surfaces having a zero contact angle with water.

Gold surfaces were obtained by vacuum depositing a thin layer (5 nm) of titanium and a somewhat thicker (15 nm) layer of gold onto silica particles and silicon wafers. The titanium layer was added to prevent gold detaching from the silicon substrate in water. The silica spheres were coated *after* they had been glued to the cantilevers. The surface roughness of the flat gold films, determined by AFM in imaging mode, was found to be less than 2 nm over an area of 1 μ m². The flat gold surface was cleaned by immersion into a "piranha solution", *i.e.*, a hot mixture of 30% H₂O₂ and concentrated H₂SO₄, for 2 minutes [15]. This resulted in a surface with a zero contact angle with water. To avoid detachment of the gold-coated particles from the cantilever, these were not cleaned with piranha solution but in a plasma cleaner (model pdc-32G, Harrick Scientific, New York, USA). Aqueous electrolyte solutions were prepared from analytical grade chemicals in deionised water (NANOpure ultra pure water, Barnstead, Dubuque, Iowa, USA; specific resistance 18 M Ω cm) and pH values were adjusted by adding aqueous solutions of NaOH or HCl.

A NanoScope III atomic force microscope (Digital Instruments Inc., Santa Barbara CA, USA) equipped with a fluid cell and a scanner "E" (12.5 μ m x 12.5 μ m) was used for the force measurements.

To avoid contamination, sample handling and mounting of the samples into the AFM was done in a laminar flow cabinet. After assembling the cantilever and wafer in the fluid cell, the cell was filled with electrolyte solution.

After each series of force measurements the spring constant of the cantilever used was determined by the "Cleveland method" as outlined in section 2.3.2. The raw force data (*i.e.*, photodiode voltage output versus substrate displacement) were converted into normalised force (F/R) versus separation curves in the way as described in section 2.5.

Streaming potential measurements on gold surfaces were performed in a parallel-plate flow cell. For a description of the experimental method and equipment to reader is referred to refs. [16, 17]. Microscope glass slides were coated with a titanium-gold layer following the same procedure as with the silica wafers. The streaming potential was measured as a function of pressure drop over the cell, in a range of pH values at a constant ionic strength of 10^{-3} M. Subsequently, the concomitant ζ -potentials of the gold surface were computed using the classical *Helmholtz-Smoluchovski equation* [18, 19]:

$$\frac{V_s}{\Delta p} = \frac{\varepsilon \zeta}{\eta K_{sp}}$$
(3.15)

where V_s is the streaming potential, Δp the pressure drop over the cell, K_{sp} the specific conductivity of the solution, and ε and η the dielectric permittivity and the viscosity of the solution, respectively. The use of this equation implies that we assume that the surface conductance (due to ions behind the plane of shear) is negligible relative to the conductance of the bulk solution. For the parallel-plate system used here, this assumption is justified, in contrast to the case of streaming potential measurements on particle plugs, where surface conductance and double layer overlap significantly affects V_s [20].

3.4 Results and Discussion

3.4.1 Force measurements between silica surfaces

Figure 3.1 shows the interaction between a silica sphere and an oxidised silicon wafer in solutions of different NaCl concentrations at neutral pH (*i.e.*, pH \approx 6). The force F between the surfaces is normalised by the radius R of the sphere.



Figure 3.1: Interaction between a silica sphere and a silica plate in aqueous solutions of various NaCl concentrations, as indicated. The data points are represented by the symbols. The curves were calculated using the DLVO theory; solid curves: constant surface potential; dashed curves: constant surface charge. The Van der Waals contribution was calculated using a Hamaker constant of $0.85 \cdot 10^{-20} J [21 - 23]$. (Results of the DLVO fits: $\psi_0 = -18 \text{ mV}$ for $10^{-1} M$, -33 mV for $10^{-2} M$, -46 mV for $10^{-3} M$, and -88 mV for $10^{-4} M$.)

For all NaCl concentrations the force curves measured on approach and on separation are identical. They show completely repulsive behaviour. As expected from electrical double-layer theory, at large separations the force decays exponentially, with a decay length which decreases with increasing electrolyte concentration.

The experimental data were fitted according to DLVO theory with the surface potential at infinite separation as the only fitting parameter. The Debye length was calculated directly from the electrolyte concentration of the solutions. To calculate the Van der Waals component of the interaction a Hamaker constant of $0.85 \cdot 10^{-20}$ J [21 - 23] was used. For each ionic strength the interaction curve was fitted under the

assumption of a constant surface potential as well as of a constant surface charge. The surface potentials at infinite separation giving the best fit to the data are given in figure 3.1.

Obviously, interaction curves from similar charged surfaces do not give information about the sign of the surface potential. However, it is well-known that the surface charge of silica is due to the association and dissociation of surface silanol groups:

SI-OH + H⁺
$$\rightleftharpoons$$
 SI-OH⁺₂
SI-OH \rightleftharpoons SI-O⁻ + H⁺ (3.16)

and the point of zero charge is around pH 2 (see, e.g., ref. [24]). Thus, at neutral pH the surface is negatively charged and therefore the surface potentials are taken to be negative.

As can be seen from figure 3.1, for separations larger than \sim 3 nm the results are in good agreement with the DLVO theory. The experimental data are in between the theoretical curves calculated for constant potential and for constant charge. Apparently, some degree of charge regulation of the silica surface takes place by protonation or deprotonation of surface OH-groups, but not to such an extent that the surface potential is constant on approach.

At small separations DLVO theory predicts that the Van der Waals attraction dominates over the electrostatic repulsion, leading to an attractive minimum as the separation approaches zero. Surprisingly, in the experimental interaction curves there is no indication at all for an attractive Van der Waals contribution. In some cases the repulsion at very small separation even *exceeds* the electric double layer repulsion. Similar deviations from the DLVO theory have been found by other researchers, not only for silica - silica interactions in aqueous salt solutions (see for example refs. [25 -28]), but also for a range of other systems such as mica - mica [29], mica - silica [28], and (dissimilar) metal sulphide surfaces [30].

There are several factors that could be responsible for the deviation of the measured interaction curves from DLVO theory at small separations. The most important ones are the surface roughness of the oxidised silicon wafer and the silica sphere, and the neglect of solvent structural forces (repulsion between hydration layers) in the theory. Since the Van der Waals forces are short-ranged, these are much smaller for rough surfaces in contact than for ideally smooth surfaces in contact; due to surface roughness the charge on the surfaces may be located at a negative surface separation,

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but this will only slightly offset the electrostatic repulsion. Grabbe and Horn [22] showed that even under conditions where the electrostatic repulsion between silica surfaces is practically zero, *i.e.*, at high ionic strength and close to the iso-electric point (i.e.p.) of silica, the Van der Waals attraction is completely obscured by a strong short-range repulsion. This repulsion can only be ascribed to hydration forces. When the H^+ of the silanol groups on the silica surfaces are replaced by ions or groups which are less successful in creating a structured water layer a (reduced) Van der Waals attraction between the surfaces is observed [31, 32].

In table 3.1 the values for the surface potentials of silica at different NaCl concentrations obtained in this work are compared to those obtained by others using various techniques. Our values are in good agreement with these literature data. Differences may be caused by differences in surface preparation of the silica. Furthermore, because the pH in some of the experiments reported in the literature was not controlled, the surface potentials may differ somewhat as a result of pH variations. The zeta-potential values obtained by Weiss *et al.* [33] tend to be somewhat higher (more negative) than the surface potentials - in fact, double layer potentials (see section 3.2) - obtained from surface force measurements. Generally, it is assumed that the ζ -potential of a solid surface in solution is approximately equal to, or somewhat smaller than the double layer potential, since the hydrodynamic shear plane is thought to be located at a distance comparable to or a little further away from the surface than where the diffuse part of the double layer starts.

lonic strength	this work*	Ducker ^a [27]	Berd* E4	Hom⁴ [26]	Peschel ^e [25]	Weiss ⁴ [33]
10 ⁻¹ M	-18	- 21		-23		-22
10 ⁻² M	-33	-34		-28		-40
10 ⁻³ M	-46	-53	-43	-32	-50.0	-67
10 ⁴ M	-88	-61		-40	-57.5	-83

Table 3.1: Surface potentials of silica (in mV) at neutral pH (pH \approx 6) as obtained from DLVO fits of the silica - silica interaction curves depicted in figure 3.1, compared to literature data.

a) colloidal probe AFM; NaCl solutions

b) Israelachvili surface force apparatus; NaCl solutions

c) self-developed force apparatus; NaCl solutions

d) zeta-potential determined by streaming potential experiments; KCl solutions

The interaction between silica surfaces was measured at different pH values in the range pH 3 - 11 at a constant ionic strength of 10^{-3} M. At every pH the force curves show features similar to those given in figure 3.1, *i.e.*, completely repulsive behaviour, which is well described by DLVO theory for separations larger than ~ 5 nm. The surface potentials at infinite separation as obtained from DLVO fits are shown in figure 3.2. As expected, with increasing the pH the surface potential becomes more negative. In this graph the potentials obtained in this work are compared to values found by Bard [34] and by Ducker [27] using colloidal probe AFM.



Figure 3.2: The surface potential of silica as a function of pH obtained from AFM force measurements. Data from this work (\bigcirc), with the total ionic strength of the solutions adjusted to 10^3 M, data from Bard (\blacksquare) [34] in 10^3 M KCl, data from Ducker (\blacklozenge) [27] in a background of 10^3 M NaCl. In all cases the surface potentials were determined by fitting force curves according to DLVO theory.

3.4.2 Streaming potential measurements on gold surfaces

Gold is the most chemically inert of all metals; the build-up of surface charge due to metal dissolution is therefore minimal. In solution the surface potential of gold is determined by specific adsorption of ions and highly dependent on the solution composition and presence of any impurities. Furthermore, the preparation and cleaning procedure of a gold surface highly affects its chemical properties (*e.g.*, presence of oxide layers) and clean gold surfaces readily adsorb contaminants from the air. It is therefore no surprise that in literature practically no consistent data on the surface potential of gold surfaces can be found. Values reported for the surface

potential of gold in neutral solutions of low salt concentration vary from +30 mV to -70 mV [27, 34, 35].

Because of the strong dependence of the double layer characteristics of a gold surface on its preparation and cleanliness and on the composition of the solution, we decided to perform streaming potential measurements on our gold films under the same conditions as applied in the AFM force measurements instead of relying on data obtained in earlier studies.

Streaming potential measurements were performed in the range pH 3 to pH 11, obtained by addition of KOH or HCl. The ionic strength of the solutions was adjusted to 10^{-3} M by adding KCl. In all the experiments a linear relationship between V_s and Δp was observed, in line with equation 3.15. A typical example is given in figure 3.3.



Figure 3.3: Streaming potential as a function of pressure drop over the flow cell for gold surfaces in a 10^3 M HCl solution. Values obtained from linear regression: offset 0.3 mV; slope 0.378 mV/cm Hg; correlation coefficient 0.998.

The ζ -potentials were calculated according to equation 3.15 and are plotted as a function of pH in figure 3.4. From this graph the i.e.p. of the gold surface is found at around pH 4.5. Apparently, the potential of the gold films strongly depends on pH. We believe that the charge on the surface stems from oxide species on the gold surface. The shape of the curve resembles that of a simple diprotic ligand, which indicates that

pH dependence is a result of a two step protonation of the oxide species. At high pH the surface is fully deprotonated leading to a negative surface charge, at the intermediate pH (around pH 7) all sites bind one proton and the oxide surface is uncharged. At lower pH all sites bind two protons leading to a positive surface charge. As can be seen from figure 3.4 the surface is not uncharged at neutral pH but has a potential of about -18 mV. This negative value is probably caused by specific adsorption of chloride ions to the surface, resulting into a shift of the complete curve of about -18 mV. The data in figure 3.4 are used to fit a 2 pK model [36, 37] with a single affinity constant for each protonation step. For this fit the dissociation constants for the gold-oxide surface are found at pH = 4.2 and at pH = 10.7.¹



Figure 3.4: Zeta-potential of the gold-coated glass slides as a function of pH (ionic strength 10^3 M). The two-step protonation is fitted to a 2 pK model. In the graph the dashed curve represents the relative concentration of protons bound to the surface. From the data fit the first dissociation constant is found to be at pH=4.2 and the second dissociation constant at pH=10.7.

The fact that streaming potentials can be measured on gold or any conductor is in itself interesting. Under influence of the pressure difference the ions in the liquid are displaced and a streaming potential is created. Because gold is an excellent conductor one might expect the charge to flow back instantaneously through the metal, thus counteracting the build-up of the streaming potential. However, in the systems studied

¹ The curve in figure 3.4 is in fact obtained by fitting the 2 pK protonation model to both the zeta-potential data set and the potentials of the gold surfaces obtained from AFM force measurements (section 3.4.3).

here, there is no effective way of charge transfer from the solution to the metal and therefore full development of the streaming potential is possible. We mention here that it has been found in our laboratory [38] that applying an electric potential across a solution, in the direction parallel to a metal plate which is in contact with the solution, gives rise to polarisation along the metal surface, rendering one end of the metal plate positive and the other end negative with respect to the solution. Above a certain value of the applied potential this results in an oxidation reaction at one end of the plate and a reduction reaction at the other end. During our streaming potential measurements a similar polarisation along the gold-coated plates occurs, but even at the highest applied pressures this polarisation is not large enough to give rise to charge transfer (by redox reactions) between the solution and the gold. If back conduction through the metal would occur, this would show up in the V_s versus ΔP plots: above a certain threshold value of V_s the slope of the lines would decrease.

3.4.3 Force measurements between gold surfaces



Figure 3.5: Interaction between a gold-coated silica sphere and a gold-coated silica surface in 10^{-3} M solutions at pH 7 (O) and pH 11 (D). The curves correspond to the electric double layer interaction calculated for the boundary conditions of constant charge (dashed curves) and constant potential (solid curves). The surface potential at infinite separation from fitting the data were -22 mV for pH 7 and -38 mV for pH 11. (Inset: the same interaction curves fitted using the DLVO theory, i.e., including Van der Waals interaction, using a Hamaker constant of $25 \cdot 10^{-20} J$ [39].)

The forces between a gold-coated silica sphere and a gold-coated silicon wafer were determined as a function of pH in solutions of NaCl with a ionic strength of 10^{-3} M. In figure 3.5 the force-distance curves are shown for pH values of 7 and of 11. For all pH

values the force at large separation decays exponentially with distance, in line with electrostatic repulsion according to DLVO-theory. As in the silica-silica force curves no attractive (Van der Waals) component is observed.

Fitting the data with the DLVO theory, using the calculated value of the non-retarded Hamaker constant for the gold-water-gold system, $2.5 \cdot 10^{-19}$ J [39], gives satisfactory results only for separation distances larger than ca 20 nm (see inset of figure 3.5). It is clear from the theoretical curves that, if this high value for the Hamaker constant would be applicable, that Van der Waals forces would dominate the last 10 - 15 nm of the approach and should - despite any hydration and surface roughness effects - be clearly visible in the experimental curves. The fact that this is not the case is in accordance with earlier observations. In most cases an attractive Van der Waals interaction for gold coated surfaces was not found [40, 41] or an attraction which was much smaller than expected [27] and could only be fitted with a much lower Hamaker constant ($3.4 \cdot 10^{-20}$ J [42], $4 \cdot 10^{-20}$ J [43]). To explain this one could reason that in these and in our measurements relatively thin gold films were used, i.e., 10 - 15 nm films on the colloidal probes and 15 - 100 nm on the flat substrates. Therefore, the effective Hamaker constant might be much smaller than the value calculated for the gold-water-gold system.

To rate this argument at its true value we calculated the Van der Waals force acting between two semi-infinite gold plates and between two gold slabs of thickness 15 nm as a function of separation distance. The results are compared in figure 3.6.

Figure 3.6 shows that for distances comparable to or smaller than the thickness of the slabs, the Van der Waals force for the two cases is of the same order. This implies that for distances < 15 nm the Van der Waals interaction between silica surfaces coated with a 15 nm gold film is approximately the same as the Van der Waals interaction between two solid gold surfaces. Therefore, the fact that thin gold films were used in the measurements instead of solid gold particles and plates, is not an explanation for the lack of any sign of Van der Waals interactions in the measured force curves. This leaves us as yet to tentatively conclude that the calculated Hamaker constant is too high. This is supported by results of coagulation experiments on gold sols [44, 45] which also point to much lower values for this constant, in the range of 1 - $6 \cdot 10^{-20}$ J. The only case - to our knowledge - that the high Hamaker constant (2.5 10-19 J) for gold surfaces was confirmed by experiment has been described by Biggs et al. [35]; this was in pure water, for small silica spheres (ca 2 µm diameter) or standard silicon nitride AFM tips covered with a 0.6 µm thick gold layer interacting with pure gold plates. These data could be fitted extremely well to the DLVO theory using the abovementioned calculated value for the Hamaker constant. In NaCl and Na-citrate

solutions, however, Biggs *et al.* [41], found only a repulsive interaction, which was attributed to specific adsorption of the anions to the gold surface, also in the separation range where the Van der Waals attraction was expected to dominate the interaction.



Figure 3.6: Van der Waals force (dashed curves; left Y-axis) plotted as a function of distance (h) for two thin gold slabs ($\delta = 15$ nm) and two semi-infinite gold plates. The unbroken curve depicts the ratio (plotted using the right Y-axis) of the two forces. This illustrates the contribution of a 15 nm gold layer to the total interaction between gold surfaces as a function of distance. The shape of this curve is independent on the layer thickness (or Hamaker constant) therefore on the lower (grey) x-axis this curve is normalised to the thickness of the layer. Note that this ratio is only valid for non-retarded Van der Waals forces.

In view of the above we decided to use just the non-linear PB equation (ignoring the Van der Waals forces) to fit the data to determine the surface potentials of the gold surfaces. This gives much more satisfactory results, see figure 3.5. The choice of the sign of the ψ_0 values is based on the i.e.p. of our gold surfaces (pH ~ 4.5) as found from the streaming potential measurements. In figure 3.7 the surface potentials obtained in this way at various pH values are given and compared to the results of the streaming potential measurements.

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Figure 3.7: The ζ -potentials (O) determined by streaming potential measurements and surface potentials (D) determined by surface force measurements. The dashed curve represent the fit to the 2 pK model with the same parameters as the fit in figure 3.4.

There is a reasonable agreement between the two data sets, the trend with pH being very similar. In comparing the data it should be realised that the force measurements were made between a gold-coated silica sphere and a gold-coated silica surface. Although the gold coatings were prepared in exactly the same way as the coating on the substrates used in the streaming-potential measurements, the cleaning procedure of the gold-coated sphere was different (*i.e.*, using a plasma cleaner, instead of cleaning with piranha solution). It cannot be excluded that the method of cleaning affects the surface structure and, hence, the surface and/or zeta-potentials.

3.4.4 Force measurements between gold and silica surfaces

The interaction between a silica sphere and a gold-coated surface was determined in the pH range 3 - 11, in solutions with a ionic strength of 10^{-3} M. The force curves at pH 3, pH 4, and pH 11 are shown in figure 3.8.



Figure 3.8: The interaction on approach between a silica sphere and a gold-coated surface in 10^3 M solutions at three pH values, as indicated. The data are fitted to the Poisson-Boltzmann equation for the boundary conditions of constant charge (dashed curves) and constant potential (solid curves). For each data set the potential of the silica surface (obtained from the silica-silica data) was entered as a parameter and the potential of the gold surface was obtained from the best fit to the data.

At pH 11, where both the silica and gold surfaces are negatively charged, the interaction clearly corresponds to electrostatic repulsion. When the pH is lowered, the electrostatic repulsion decreases, as expected. At pH 4 a small but distinct maximum in the force curve is observed at a separation of 3 - 4 nm, comparable to what Toikka

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et al. [30] have found for the interaction between dissimilar metal sulphide surfaces. At pH 3 the interaction force is practically zero for separations larger than ca 8 nm; at smaller separations the interaction is attractive.

The experimental curves are compared to numerical solutions of the non-linear PB equation for surfaces interacting at the constant charge and constant potential extrema ('best fits'). No Van der Waals term was added, since in none of our silica-silica and gold-gold interaction curves any indication was found for Van der Waals forces. The surface potentials of silica as obtained from fits of the silica-silica interaction curves were used as input parameter in the calculations.

The experimental curves are well within the calculated extrema of constant charge and constant potential. From the measurements on the symmetrical systems (see figures 3.1 and 3.5) it is already clear that neither of the surfaces is maintaining constant charge or constant potential on approach. In other words, on both the silica and the gold surface some degree of charge regulation occurs. The calculated curves clearly illustrate that it is much more crucial to know more about the mechanism of charge regulation for describing the interaction between dissimilar surfaces than for the interaction between two identical surfaces. A rigorous charge regulation model has been developed, for example, by Grabbe and Horn [21 - 23], but to apply this it is necessary to know more about the charge regulation mechanism, otherwise one ends up with to many unknown parameters.

Since we have not enough knowledge on the details of the charge regulation, we are limited to the long-range part of the interaction curves where the extrema (both surfaces of constant potential or both surfaces maintaining constant charge) still coincide to obtain values for the surface potentials. This is only a limited range of separation distances (larger than, say, 20 nm) where the interaction force is low, in particular at pH 4 and pH 3. Furthermore, the value obtained for the potential of the gold surface is extremely sensitive to the input value for the potential of silica. With respect to this we note that the silica-silica system from which these input parameters are derived is not entirely symmetric; there may be differences between the potential of the silica probe and the oxidised silica wafer [28].

In view of the above it is not surprising that the surface potentials at infinite separation of the gold films obtained from the fits in figure 3.8 deviate from the values obtained from the gold-gold interaction curves and from the zeta- potentials obtained from the streaming potential measurements. See table 3.2.

	zota-potential	gold-gold	silica-gold
11	-54	-38	-26
4	+7	+27	-13
3	+16	+50	+10

Table 3.2: Potentials of the gold surface (in mV) as obtained from streaming potential measurements, and fitting of gold-gold and silica-gold interaction curves with the non-linear PB equation.

At pH 11 the double layer interaction is strongest, but there is a large variation in the values for the surface potential obtained from the different measurements. At pH 3 the potential obtained from the silica-gold interaction is in reasonable agreement with the zeta-potential of the gold surface, which is probably the best value to compare with. (The zeta-potential was measured for a gold surface prepared and cleaned in the same way as the gold surface used in the silica-gold force measurements; in the gold-gold force measurements the surface of the gold-coated sphere was cleaned in a different way, see section 3.3.) The measured interaction between silica and gold at pH 4 would imply that the gold surface has a (small) negative potential at this pH, which is not in line with the measured positive zeta-potential of the gold films under the same conditions. The calculated curves in figure 3.8 nicely illustrate the behaviour of electrostatic interactions between dissimilar surfaces. For surfaces of the same charge sign, both maintaining constant charge, the interaction is always repulsive (dashed curves in figures 3.8a,b); if they maintain constant potential, the repulsion turns into an attraction on approach (solid curves in figure 3.8a,b) as a result of charge reversal on the surface with the lower potential (this has been experimentally observed by Toikka et al. [30]). For surfaces of opposite charge signs, maintaining constant potential, the interaction is always attractive (solid curve in figure 3.8c); for constant charge surfaces of opposite sign, the attraction turns into a repulsion on approach (dashed curve in 3.8c). The more extreme the ratio between the surface charge densities at infinite separation, the larger the separation distance at which reversal of the interaction occurs. In the experimental curve measured at pH 4, where the ratio of the charge densities of the gold and silica surfaces is small, the bump at 3 - 4 nm probably reflects the onset of a change of repulsion into attraction; before the sign of the electrostatic interaction on approach really changes from positive to negative, other effects (such as hydration) start to dominate the force curve. The small maximum in the curve is not likely to be due to a Van der Waals contribution, as we have not found evidence for Van der Waals attraction in any of the other force curves.

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3.5 Conclusions

In this chapter force measurements between silica surfaces, gold surfaces and a silica and gold surface in aqueous solutions have been described. For all systems investigated the force-distance curves are dominated by electrostatic interactions at separations larger than a few nanometres. The experimental data are in between the (fitted) theoretical curves for the boundary conditions of constant charge and constant potential, respectively. Apparently, both the silica and the gold surface are subject to some degree of charge regulation. For the silica surface, charge regulation proceeds mainly by protonation or deprotonation of surface silanol groups; the charging mechanism of the gold surface depends on how the gold surface was prepared and cleaned, and on solution conditions and presence of impurities. Under the experimental conditions applied here, the potential of the gold is partly determined by the solution pH, probably due to the presence of oxides on the surface. Furthermore specific adsorption of Cl⁻ ions seems to play a role in the charging mechanism.

In none of the measured interaction curves evidence was found for an attractive Van der Waals component. Although this is surprising, it is in line with what is generally reported in literature. In the case of silica-silica interactions, the Van der Waals forces may be obscured by non-DLVO short-range interactions, in particular hydration forces, and by surface roughness effects. For the gold-gold interaction, however, the literature value for the Hamaker constant is so large that Van der Waals forces should definitely be noticeable in the force curves. Yet, there is no indication of Van der Waals attraction in the experimental force curves. Why this is so, is not clear. Perhaps, the literature value for the Hamaker constant (a calculated value) is incorrect; this is corroborated by the fact that in most cases found in literature a much lower Hamaker constant in needed to explain the interaction between gold surfaces (in force measurements as well as in coagulation experiments).

By fitting the experimental curves according to the DLVO theory or simply to the nonlinear PB equation (i.e., leaving out the Van der Waals forces) the potential of the surfaces at infinite separation was determined. The potentials obtained for the silica surface (at various electrolyte concentrations and over a range of pH values) are in good agreement with values reported in literature. The potential of the gold surface as a function of pH obtained from fitting the gold-gold interaction curves agrees reasonably well with the zeta-potential obtained from streaming potential measurements. This shows that we can successfully carry out surface force measurements using an AFM.

The potentials of the gold surface at various pH values (pH 11, 4 and 3) were also obtained from fitting silica-gold interaction curves to the non-linear PB equation,

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using the potentials of the silica surface as input parameter. The results deviate from those obtained from the gold-gold interactions, in particular at pH 4, where a (small) negative surface potential is found instead of a positive value. Determination of the surface potential from interaction curves of dissimilar surfaces is more difficult than from symmetrical cases. In the symmetrical case the charge densities and the degree of charge regulation on the two surfaces are, of course, the same and the electrostatic interaction is always repulsive. Furthermore, over a large separation range the solutions of the PB equation under conditions of constant charge and constant potential are not very different. For dissimilar surfaces, however, there is a huge difference between the solutions of the PB equation for both surfaces at constant charge or both surfaces at constant potential. Without detailed knowledge on the charge regulation mechanisms (including characteristic time constants!) only the part of the experimentally determined interaction curve at large separations can be used for fitting the potential of one of the surfaces, the potential of the other surface being given. Another consequence is that it is virtually impossible without a rigorous charge regulation model to quantify non-electrostatic interactions by subtracting the electrostatic component from the total measured force.

3.6 References

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Forces Between Polymer-Covered Surfaces¹

Abstract: An atomic force microscope was used to measure the interaction forces between a polymer-covered silica sphere and a polymer-covered silica plate at various pH values and electrolyte concentrations, and for different polymer chain lengths. The polymer used is poly(ethylene oxide) (PEO). The force measurements were performed in aqueous solution without dissolved polymer, at scan rates corresponding to the velocity of Brownian collisions between dispersed colloidal particles. In all cases the repulsion on approach was found to be electrostatic in nature; although the PEO adsorption layers are saturated, there is no sign of steric repulsion before the distance of closest approach between the silica surfaces is reached. At pH 4 the approach curves show for separations smaller than 20 nm an attractive component that partly compensates the electrostatic repulsion. On retraction a strong adhesion is observed, which is attributed to bridging. At pH 8 and low electrolyte concentration (10-3 M NaCl) the interaction is repulsive on approach and on retraction; no adhesion by bridging takes place. However, upon increasing the NaCl concentration a weak adhesion is induced. At an intermediate pH of 6.5 the adhesion on separation depends on the force with which the surfaces have been pressed together (10^{-3} M NaCl). The pH-dependence of the interaction curves is discussed in terms of the segmental adsorption energy of PEO on silica, which is known to decrease with increasing pH. Measurements at pH 4 show a strong dependence of the adhesion force on the chain length. A linear relationship between the adhesion force and the surface coverage (in mass per unit area) is found and adhesion occurs only for chain lengths above a certain threshold value.

¹ The results described in this chapter have been published in a paper entitled : Forces between polymer-covered surfaces; a colloidal probe study. *M. Giesbers, J. M. Kleijn, G. J. Fleer, M. A. Cohen Stuart, Colloids Surfaces A, 142 (1998) 343.*

4.1 Introduction

When polymers are adsorbed onto colloidal particles various effects on the stability of their suspensions can be expected, ranging from steric stabilisation to bridging flocculation, depending on the polymer conformation at the surface [1]. Polymers at interfaces play an important role in many industrial products and processes. For example, they may act as stabilisers in paints and in pharmaceutical and cosmetic creams, and play an important role in the production of magnetic tapes, fluorescent lamps, and television screens. The flocculation by polymers is exploited in, for example, water purification, mineral processing and paper manufacturing. Polymers at interfaces are also applied in adhesives, coatings and (polymer) composites. In these applications the strength of the polymer surface contact is a decisive factor.

Considering the complexity of the interactions between polymer-covered surfaces and the technological importance of control of the stability of colloidal suspensions, it is not surprising that these interactions have been the subject of many studies (see, for example, Refs. [2 - 14].

Using the AFM we investigate the interaction between colloidal particles and flat surfaces under various experimental conditions in order to determine the influence of polymers and (functional) surface groups on adhesion. In this chapter we present a study on the interaction between two polymer-covered silica surfaces in electrolyte solutions. The polymer is poly(ethylene oxide) (PEO), of several molecular weights. Experiments were performed at different pH values and at varying background electrolyte concentrations. In most cases, the surfaces were brought together at a rate comparable to that for a Brownian collision (a discussion about this is given at the end of this chapter). We expect therefore that the observed force-distance curves are representative for the interactions between colloidal particles in a dispersion.

PEO is an uncharged homopolymer and is available in fractions with a narrow molecular weight distribution. Its adsorption behaviour on silica has been studied extensively [15 - 22]. The rate of adsorption of PEO is largely determined by the mass transfer between bulk solution and surface, because of the rapid equilibration of the adsorbed layer [18]. This rapid adaptation of adsorbed PEO is probably caused by the high flexibility of the polymer chain, enabling a fast reconformation during the adsorption process. The effective segmental adsorption energy χ_s of PEO on silica can be varied by changing the pH [17]. It has been shown both theoretically [1, 23] and experimentally [5, 16, 17] that the adsorbed amount and hydrodynamic layer thickness are only slightly affected by the adsorption energy χ_s . Especially the hydrodynamic layer thickness δ_h is nearly constant over a wide range of adsorption energies, and pH

values. Only when χ_s becomes very small, close to the desorption point, δ_h falls off sharply to zero; in the case of PEO/silica this occurs around pH 10.5.

The interaction between PEO-covered mica surfaces in 0.1 M KNO₃ was studied before by Klein and Luckham [2, 3] using the surface force apparatus (SFA). At full coverage of the surfaces they observed steric repulsion. The range of interaction was reported to be typically in the order of no less than five times the radius of gyration of the polymer. At low surface coverages, bridging attraction was observed. More recently, the interaction between glass (silica) surfaces with adsorbed PEO of different molecular weights in 0.2 M KNO₃ solutions was studied by Braithwaite and Luckham [9, 10] using a home-built AFM. Their results were virtually the same as found earlier for the interaction between PEO-covered mica surfaces with the SFA.

4.2 Experimental

The silica spheres were a gift from Philips Research Laboratories (Eindhoven, The Netherlands). The diameter of the spheres is 6 μ m. Silicon wafers were oxidised to a depth of 100 nm to give flat silica surfaces. The roughness of the oxidised wafers, determined by AFM in imaging mode, was found to be about 2 nm over an area of 1 μ m².

Poly(ethylene oxide) (PEO) polymers, with molecular weights of 23, 56, 105, and 246 kg/mol, were obtained from Polymer Laboratories Ltd (Shropshire, UK). Some properties of the polymers are listed in table 4.1. All other chemicals used were of analytical grade and used without further purification. Water was purified with a NANOpure ultra pure water system (Barnstead, Dubuque, Iowa, USA); the resulting specific resistance was at least 18 M Ω cm.

A NanoScope III atomic force microscope (Digital Instruments Inc., Santa Barbara CA, USA) equipped with a fluid cell and a scanner "E" (12.5 x 12.5 μ m) was used for the force experiments. The technique of measuring forces with the AFM has been described in chapter 2.

For all experiments standard silicon nitride cantilevers (Digital Instruments Inc., Santa Barbara CA, USA) were used. The spring constants of the cantilevers were measured by means of the "Cleveland" method (see section 2.3).

The silica spheres were glued onto the cantilevers under an Olympus microscope and using a three-way translation stage. The glue used for this purpose was Epikote 1004 (Shell, Amsterdam, The Netherlands). The cantilevers with silica spheres and the silica wafers were cleaned in a plasma cleaner (model pdc-32G, Harrick Scientific, New York, USA) just prior to the experiments.

Sample handling and mounting of the samples into the AFM was done in a laminar flow cabinet to avoid contamination. After assembling the cantilever and wafer in the fluid cell, the cell was filled with electrolyte solution and the repulsive silica-silica interaction was measured to check for clean surfaces. Subsequently, a PEO solution of 100 mg/l of about pH 6.5 was injected into the cell. The polymer solution was left in the cell for 20 minutes to allow the formation of a polymer layer onto the silica surfaces.

Finally, the polymer solution was replaced by aqueous solutions of given pH and ionic strength in which the actual force measurements were made. All solutions had an ionic strength of 10^{-3} M (NaCl) unless stated otherwise.

Molecular weight, M _w (kg/mol)	polydispersity (M _w /M _n)	radius of gyration ^{a)} (nm)	chain length ^{b)} (nm)	hydrodynamic layer thickness ^{c)} (nm)
23	1.08	5.1	170	3.7
56	1.05	8.1	420	5.7
105	1.06	11.1	780	7.8
246	1.09	17.0	1800	11.8

Table 4.1: Characteristics of the PEO molecules used

a) calculated radius of gyration for unperturbed random coils in aqueous solution.

- b) for a completely stretched chain, calculated from the molecular weight.
- c) hydrodynamic layer thickness of PEO adsorbed on silica (saturated layers), from Van der Beek and Cohen Stuart [17].

4.3 Results

4.3.1 Polymer-covered silica surfaces: pH dependence

In figures 4.1 - 4.3 force curves for PEO-covered surfaces ($M_w = 246$ kg/mol) at different pH values are shown. It should be kept in mind that all separations are relative to the distance between the surfaces at constant compliance, i.e., at "zero

separation" the two polymer adsorption layers are sandwiched between the silica surfaces. The distance of closest approach is thus not known exactly.



Figure 4.1: Force between two PEO-covered silica surfaces at pH 4. Molar mass of PEO is 246 kg mol¹, and the NaCl concentration is $10^{-3}M$. Circles represent the approach curve, squares represent the retraction curve. Positive values of F/R correspond to a net repulsion. Inset: detail of the approach curve compared to that for bare silica surfaces.

At pH 4 the force curves for PEO-covered surfaces (figure 4.1) show a behaviour which is quite different from the interaction between bare silica surfaces. On approach the interaction is repulsive and this repulsion is probably electrostatic in nature, as indicated by the resemblance with the interaction curve for bare silica surfaces at large separations (see inset in figure 4.1)¹. Only at small separations (< 20 nm) the approach curve for PEO-covered surfaces starts to deviate from that for bare silica surfaces, indicating that some attractive component is present. Upon separation of the surfaces after contact there is a strong adhesion and at a certain

¹ In the inset of figure 4.1 (and also in figures 4.2b and 4.2a) the force-distance curves for bare silica surfaces and for PEO-covered silica surfaces are presented together with the same distance axis. In fact, the curves for PEO-covered silica should be shifted and start at a distance of twice the thickness of the compressed polymer layers. However, this distance is not precisely known. The only purpose of this way of presentation is to show that the (long-range) interaction on approach between the PEO-covered surfaces is governed by electrostatic repulsion.



Figure 4.2: A) As figure 4.1, but for pH 8. B) Approach curves (\bigcirc) on a log/lin scale compared to the approach curve for bare silica surfaces (\Box) at the same pH and electrolyte concentration.

point the surfaces rapidly jump apart ("pull-off") to about 225 nm separation. Unfortunately, neither the pull-off distance nor the value of the adhesion force just before pull-off could be measured due to the limited range of cantilever deflection the apparatus can detect.



Figure 4.3: A) Approach curve for PEO-covered silica surfaces at pH 8 at different concentrations of NaCl. Molar mass of PEO is 246 kg mol⁻¹. B) Retraction curves.

At pH 8 (figure 4.2) the force curves for approach and for retraction coincide and are completely repulsive. These curves are practically identical to those for the bare silica surfaces at the same pH and electrolyte concentration. When we changed the pH in the cell to pH 4, we obtained the same interaction curves as measured before at pH 4. When the solution of pH 8 is replaced by solutions of higher NaCl concentration (of the same pH), the electrostatic interactions are screened and the decay length of the repulsive force on approach decreases as expected (figure 4.3a). Upon separation of

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the surfaces now an adhesive force is observed, the magnitude of which depends on the electrolyte concentration (figure 4.3b).



Figure 4.4: Interaction between two PEO-covered silica surfaces at neutral pH (~ 6.5) at various load forces (raw data). Molar mass of PEO is 246 kg mol⁻¹, and the NaCl concentration is 10^{-3} M.

In contrast to our observations at pH 4 and pH 8, we found that at pH 6.5 the interaction curves are highly dependent on the load force, i.e. the force with which the surfaces are pressed together. This force is increased by enlarging the constant compliance region. In figure 4.4 we do not give force-distance curves, but we present the raw data (cantilever deflection versus piezo position). For low load forces the interaction between the PEO-covered surfaces is completely repulsive, as at pH 8. When the load force is increased, however, an adhesive force is observed on retraction.

By enlarging the constant compliance region not only the load force, but also the contact time of the polymer-covered surfaces is increased. To determine whether the adhesion was introduced by the prolonged interaction time or simply by the higher load force, we also investigated the time effect on the interaction curves by varying the frequency of approach and retraction from 10^{-3} Hz to 40 Hz. However, this did not have any effect on the shape of the curves.

4.3.2 Polymer-covered silica surfaces: chain-length dependence

We repeated the experiments at pH 4 with PEO of various chain lengths (figure 4.5). The interaction curves for each of the PEO samples show the same features: a repulsive approach of electrostatic nature which is, at small separations, partly compensated by an attractive component, and an adhesive force on separation of the surfaces. As before, at this pH we observed no load-force dependence in the interaction curves.



Figure 4.5: Force between two silica surfaces covered with PEO of various chain lenghts at pH 4 and a ionic strength of 10^{-3} M. Circles represent the approach curves; squares represent the retraction curves. Molar mass of PEO = 23 kg mol⁻¹ (A); 56 kg mol⁻¹ (B); 105 kg mol⁻¹ (C); 246 kg mol⁻¹ (D).

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The magnitude of the adhesive force clearly depends on the chain length of the polymer. For the smallest PEO molecules (23 kg/mol) (figure 4.5a) the adhesion is strongest at a separation of about 12 nm. Upon further retraction there is a gradual release and at 35 nm the surfaces spring apart, as indicated by a small jump to zero force. For the PEO molecules with higher molar masses (figures 4.5b,c,d) the maximum adhesive force was too large to be measured directly. In these cases there is no gradual release, but the surfaces are torn apart as soon as the deflection of the cantilever times its spring constant exceeds the adhesive force. However, we can make a reasonable estimate for this "pull-off force" using the value obtained by extrapolating the path of the surfaces springing apart to the force axis. In figure 4.6 the thus obtained pull-off force is given as a function of the molecular weight of the adsorbed polymers.



Figure 4.6: Pull-off force as a function of the molecular weight of the PEO chains adsorbed at the silica surfaces at pH 4 and 10^{-3} M NaCl. For $M_w = 23$ kg mol⁻¹ the maximum adhesive force is given.

4.4 Discussion

As already mentioned in the introduction to this chapter, the effective adsorption energy of PEO on silica decreases gradually with increasing pH [17]. Nevertheless, the adsorbed amount of PEO on silica is roughly constant up to pH \approx 8 and then falls off to zero in the pH range 8 - 11 [5, 17]. Also from our measurements it follows that, although the interaction between PEO-covered silica surfaces at pH 8 differs from that at pH 4, the adsorbed amounts at these two pH values are not much different. Switching solutions in the cell from pH 8 to 4 and vice versa gives the same interaction curves as measured directly after adsorption. This implies that no desorption of PEO takes place by increasing the pH from 4 to 8.

At pH 4 and 10⁻³ M NaCl the approach curve is dominated by electrostatic repulsion between the silica surfaces (figure 4.1). Only when the surfaces come close, does an attractive component decrease the repulsive force. Subsequently, on separation, there is a strong adhesive force. We attribute this attractive component and adhesion to *bridging*. On first sight, this may seem somewhat surprising, since usually bridging is only found for undersaturated surfaces [1]. Under the conditions of our experiments maximum adsorption of PEO must have taken place. The applied PEO concentration of 100 mg l⁻¹ is well within the plateau region of the adsorption isotherm of PEO on silica [16, 17]. Before each experiment the adsorption time was at least 20 minutes. Reflectometer experiments by Dijt et al. [18] show that, under appropriate flow conditions, the maximum adsorption of PEO on silica is reached within 40 s. Furthermore, in a number of cases we followed the adsorption in the cell by measuring force curves at regular time intervals to make sure that a steady state was achieved before we moved on to the actual measurement of the interaction curves.

Despite the fact that the PEO adsorption layers are presumably saturated, there is no sign of steric repulsion before constant compliance is reached, and it appears that it is still possible for the polymer chains adsorbed at one silica surface to attach to the other silica surface. This may be explained as follows. Upon approach the concentration of the polymer segments between the surfaces increases. Due to the flexibility of the PEO chains, fast reconformation of the adsorbed layers can take place, and additional adsorption of polymer segments is possible. Some of the newly formed PEO/silica contacts are bridging contacts. From the observation that attraction (or better, partial compensation of the electrostatic repulsion) occurs already on approach and that the interaction curves do not change with scan rate, we conclude that on the time scale of the experiments the conformation of the polymer layers can indeed adapt to the changing conditions. At pH 4 the segmental adsorption energy is high and desorption of the segments is relatively slow [4]. Upon separation, the chains first have to be stretched to some extent before the bridging contacts are broken.

At pH 8 there is a stronger electrostatic repulsion between the silica surfaces than at pH 4 (the point of zero charge of silica is at pH 2 - 3 [24]) and the effective adsorption energy of PEO on silica is lower than at pH 4. At this high pH and at low electrolyte concentration (10^{-3} M NaCl), the force curves on approach and on separation show no hysteresis and they are completely determined by double layer repulsion between the silica surfaces (figure 4.2). Under these circumstances bridging is negligible; if any bridges are formed at all, they are so weak that they are broken immediately when the

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surfaces are separated again. Increasing the electrolyte concentration does not only result into more effective screening of the electrostatic repulsion between the silica surfaces, but adhesion starts to develop as well (figure 4.3). We speculate that the bridging occurs only when the surfaces are pressed together enough to trigger the formation of bridging contacts. At pH 8 the stronger electrostatic repulsion causes that the surfaces cannot be pressed together enough to induce this bridging. When the electrolyte concentration is increased, however, the electrostatic repulsion becomes less and bridging can once again take place.

The behaviour of the system at pH 6.5 (figure 4.8) can be explained in much the same way. It is an intermediate case between the situation at pH 8, where no significant bridging occurs (at least not at 10^{-3} M NaCl) and that at pH 4, where adhesion is strong. Only at this intermediate pH of 6.5 an effect of the load force is observed. At pH 8 we were able to initiate briding by decreasing the repulsive force. Here we are able to do much the same thing but not by decreasing the opposing force (the electrostatic repulsion) but by increasing the force with which the surfaces are pressed together (the load force).

Using essentially the same technique as applied here (but with much larger particles, 120 μ m in diameter), Braithwaite and Luckham [10] observed bridging between PEO-covered silica surfaces for partly covered surfaces, but not for fully covered surfaces. At present, the reasons for the difference with our results is not clear. In any case, the experimental conditions were different: they measured in 0.2 M KNO₃ and at neutral pH, and (in the case of full coverage) with PEO present in the solution. From our results, it is seen that both the pH and the electrolyte concentration have a pronounced effect on the force-distance curves. Our data show some relation with those of Lafuma et al. [5] on the bridging of colloidal silica particles by PEO polymers. These authors reported weak, attractive interactions between silica particles with saturated PEO adsorption layers at pH 8 ~ 9. Under shear or by adding salt these attractions generate transient flocs or very loose aggregates. In both cases, some bridging can explain the results.

In contrast to Klein and Luckham [2, 3] and Braithwaite et al. [9, 10] who observed interaction between PEO adsorption layers on mica and silica surfaces already for distances of the order of several times the radius of gyration of the polymer chains, we see an effect of the PEO chains on approach only in the last 25 nm. Considering the fact that the hydrodynamic thickness of an equilibrated adsorption layer of 246 kg/mol PEO is only about 12 nm (see table 4.1), in combination with the observation that at "zero separation" the actual distance between the silica surfaces corresponds to the thickness of the two compressed layers, our results seem to be quite reasonable. Also

in other studies [5, 25] it was found that the range of interaction between adsorbed polymer layers is only slightly larger than twice the hydrodynamic thickness of the adsorbed polymer layers.

On retraction, when bridges have been formed, the chains become stretched and the adhesion acts over a longer range than the interaction between PEO layers on approach. Only in the cases of relatively weak adhesion the polymers are gradually released from one of the surfaces and the range of adhesion forces is experimentally accessible: for the smallest PEO chains (23 kg/mol) at pH 4 it is about 35 nm (figure 4.5a), for the largest PEO chains (246 kg/mol) at pH 8 it is about 150 nm (figure 4.3b). These values seem reasonable considering the chain lengths for the completely stretched polymers, 170 and 1800 nm, respectively (table 4.1). We suggest that this process of gradual release involves rearrangements leading to longer bridges (of more segments).

When the adhesion is strong, the force needed to induce desorption of PEO trains on the surface is higher and therefore a gradual release does not occur. We take this as a strong indication that the number and length of the bridges remain constant under retraction. Only at the moment when the force exerted on the chains becomes larger than the adhesion force all bridges "snap off" at once and the surfaces are separated instantaneously.

The approach curves at pH 4 do not significantly depend on the molar mass of the adsorbed PEO layers (figure 4.5). (However, an accurate analysis would probably show that the range of interaction between both adsorbed layers before contact increases with the hydrodynamic radius.) The adhesion upon separation shows a much more pronounced dependence on PEO chain length (figures 4.5 and 4.6). In order to interpret these features we present the following tentative picture. The plateau adsorbed amount of PEO on silica increases with the chain length of the polymers [18]. This increase in adsorbed amount gives rise to more extended loops and tails, as reflected by the larger hydrodynamic radius of the adsorption layer (table 4.1), while at the same time the number of segments directly bound to the surface (in trains) is more or less constant [1]. Therefore, we expect that the adhesion force is approximately linear in the adsorbed amount per unit area, since it is mainly the loops and tails which are involved in the formation of bridges. Using data of Dijt et al. [18] for the plateau adsorbed amounts of PEO on silica as a function of the molecular weight of the polymer, we constructed figure 4.7. In this picture, the adhesion force is plotted as a function of the adsorbed amount of polymer. Indeed, a linear relationship is found. A minimum chain length is necessary to obtain adhesion by bridging, since part of the chains is necessary for anchoring to the surfaces; therefore the line in figure 4.7 has a

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finite off-set. It should be noted that the relation between adhesion force and chain length depends highly on pH and electrolyte concentration.



Figure 4.7: Relation between the adhesion between two PEO-covered silica surfaces at pH 4 and 10^3 M NaCl and the plateau adsorbed amount of PEO for different chain lengths.

Most of the measurements reported here were done at a scan rate of 1 Hz. At this scan rate and with a typical scan size of 500 nm, the surfaces are driven together at a rate of 1 μ m/s. The diffusion coefficient of colloidal particles of 300 nm diameter in aqueous solution is approximately 1.4 x 10⁻¹² m²/s. This corresponds to a RMS displacement of 1.4 μ m/s. Hence, the scan rate applied here corresponds approximately with actual collision velocities in colloidal dispersions. Therefore, the measured force-distance curves may well be representative for the interaction between colloidal particles in solution. This does not necessarily imply that under the circumstances where we observed bridging, such bridging will also occur in colloidal dispersions. An essential difference between force measurements and Brownian collisions in colloidal dispersion is that in the former case the surfaces are forcibly pushed together, whereas in a dispersion such "push" is absent; in a dispersion the electrostatic repulsion between the silica surfaces might prevent bridging flocculation, depending on the ratio of the range of electrostatic interaction and the thickness of the polymer layers (see also Ref. [4]).

4.5 Conclusions

In this study the interaction between PEO-covered silica surfaces was investigated at different pH values and electrolyte concentrations, and as a function of PEO chain lengths. In all cases the repulsion observed on approach was of an electrostatic nature. Even though the surfaces were fully covered with polymer, no indication was found for steric repulsion before the distance of closest approach was reached. In a number of cases an adhesive force was observed upon retraction, which we attribute to polymer bridges formed when the surfaces come into close contact.

At pH 4, the main interaction upon approach is electrostatic repulsion, but for small separations an attractive component shows up. The range of interaction between the adsorbed PEO layers is in the order of twice their hydrodynamic thickness, which seems to be more plausible than an interaction range of several times the radius of gyration of the polymers in solution, as reported in literature [2, 3, 9, 10]. However, the distance over which the PEO layers interact, and the thickness of the compressed polymer layers could not be determined accurately. This uncertainty remains one of the drawbacks of an AFM-like technique to measure surface forces. On the other hand, an advantage of the AFM above the SFA is that interactions can be measured on a time scale which is relevant for Brownian collisions in colloidal dispersions.

The adhesion force due to bridging between the polymer-covered surfaces decreases with increasing pH (at constant electrolyte concentration). This effect can be understood from the decreasing segmental adsorption energy with increasing pH. PEO is believed to adsorb onto silica by the formation of hydrogen bonds between its ether oxygens and surface silanol groups [17]. With increasing pH more surface silanols become dissociated and the polymer does not bind to these dissociated groups. At 10⁻³ M NaCl the force needed to separate the surfaces after contact is relatively high at pH 4. At pH 6.5, however, the adsorption energy is already decreased somewhat, enough to find adhesion only at high load forces. At pH 8 adhesion does not take place at all. We think that the electrostatic repulsion at this pH prevents the surfaces to be pressed together enough to induce bridging (at the load-forces we used). When the electrolyte concentration is increased the repulsion is screened and bridging can occur.

4.6 References

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Interactions between Acid- and Base-functionalised Surfaces

Abstract : Silica and gold-coated silica surfaces - particles and plates - were modified with self-assembled monolayers with either amine end groups or carboxylic acid end groups. The silica surfaces were modified with 3-amino-propyltriethoxysilane and the gold-covered surfaces with 11-mercapto undecanoic acid. The layers were characterised by contact angle measurements and streaming potential measurements. Streaming potential measurements showed that for the silane-amine layers the density of the surface groups depends strongly on the pretreatment of the silica surfaces. Furthermore, over a long period of time the amine layers are not stable; the zetapotential of the silane modified surfaces drops to half of its original value in 10 - 35 hours, depending on the pretreatment. The carboxylic thiol layers on gold are much more stable and show only little degradation in time. Force measurements using colloidal probe AFM were performed on these surfaces in aqueous environment as a function of pH and ionic strength. Upon approach the interaction is dominated by electrostatics. No evidence was found for Van der Waals forces. On retraction a pH dependent adhesion is measured for all combinations of modified surfaces studied. In the case of NH₂-COOH interaction this adhesion is attributed to acid-base interactions, for NH₂-NH₂ and COOH-COOH interaction to H-bonding. The work of adhesion is relatively small - as compared to literature data-, probably due to surface roughness which reduces the physical contact area.

5.1 Introduction

Interactions between surfaces with terminal acid or base groups are of special interest since their properties, e.g., the surface charge or potential, can be easily varied by varying the solution parameters. Control over the electrostatic and acid-base interactions between surfaces is an important means in controlling colloidal stability or adhesion phenomena. Acid-base interactions also play a crucial role in living systems, for example in the structure and structural stability of proteins and in the cohesion between DNA strands.

Electrostatic forces operate over a relatively long range, whereas acid-base interactions act typically at intermolecular distances of about 0.2 - 0.3 nm, when the surfaces are essentially in contact. Unlike electrostatic and London dispersive interactions, acid-base interactions are specific. In acid-base interactions covalent bonds are formed between base groups which donate an electron pair and acid groups accepting this electron pair. The hydrogen bond may be considered as a special kind of acid-base interaction: it is not a true covalent bond, but it possesses the same characteristics in that it is rather strong and directional. The formation of hydrogen and acid-base bonds is exothermic and their energy is between 10 and 40 kJ mole⁻¹[1,2].

In this chapter we investigate the influence of functional surface groups on the adhesion of colloidal particles to macroscopic surfaces. Interactions between two carboxyl functionalised layers, between two amine layers and between amine and carboxyl layers were studied as a function of the ionisation of the functional groups. The acid and base surfaces were prepared using self-assembled monolayers of thiols on gold or silanes on silica.

5.2 Self-assembled monolayers

5.2.1 Introduction

Self-assembled monolayers (SAMs) are highly organised monolayers that are formed spontaneously by chemisorption of molecules from solution or from the gas phase onto a surface. Surfactant molecules capable of forming self-assembling layers can in general be considered to consist of three parts, as illustrated in figure 5.1. The first part is the headgroup which couples the surfactant molecule to the surface through a chemical bond. This bond can be a covalent bond or an ionic bond. The chemisorption enthalpy involved in the self-assembly is about 130 kJ mole⁻¹ in the case of alkanethiols on gold [3] and is independent of chain length. Due to this high binding

energy the molecules will try to occupy every available binding site. This can only be achieved when the molecules push each other into a highly ordered array.

The second part of the self-assembling molecule is the alkyl chain. Although SAMs are not limited to long chain molecules the length of the chain does play a role in the organisation of the layer. In the ordered monolayer the loss of free energy due to the reduced entropy is partly compensated by Van der Waals interactions between densely-packed chains and in aqueous solutions also by hydrophobic interactions.



Figure 5.1: Schematic representation of molecules in a self-assembled monolayer (SAM).

The third part of the molecule is the terminal functional group. The structure of the self-assembled layer is not affected by the terminal functional group provided this is not larger than the cross-sectional area of the alkyl tail [4]. By varying the terminal functional group, surfaces with different chemical properties can be obtained.

Several types of self-assembled monolayers have been described. Examples are monolayers of fatty acids on aluminium oxide [5-7] or on silver [8], silane derivates on silica [9-12] or on mica [13, 14], or alkanethiols on gold [15-19].

In this work monolayers were formed by adsorption of silane compounds from aqueous solution onto silica and adsorption of alkanethiol compounds dissolved in ethanol onto gold.

5.2.2 Silane layers

Silane molecules may form self-assembled monolayers on hydroxylated surfaces such as silica (SiO₂). During adsorption onto silica the hydrolysis reaction of the terminal group (-SiCl_x for chlorosilanes or -Si-(O-C_nH_{2n+1})_x for alkoxysilanes, where x=1,2,3

and n usually 1 or 2) with the surface silanol group (Si-OH) leads to covalent siloxane bonds (Si-O-Si). The reaction can take place from the vapour phase or from a solvent. Vapour phase deposition, where the silane molecule reacts directly with the hydroxylated surface, leads to better-ordered monolayers [20]. Deposition from the vapour phase, however, can generally only be done at high temperatures (>100°C). Modification in solution at ambient temperature puts less strain on the samples and the thermal stability of the silane is less important. Therefore, the modification is usually done from solution. In this case the silane does not directly couple to the surface. First it is hydrolysed to silanol after which it is adsorbed via hydrogen bonding. This silanol reacts with a surface silanol groups forming a siloxane bond. The water needed for hydrolysis of the silane compound is either present as a monomolecular water layer on the hydroxylated surface or in small amounts in the solution. Under strict water-free conditions no reaction occurs between the silane and the silica surface [21].

SILANE COMPOUNDS

>O-CH2CH3 H2NCH2CH2CH2Si-O-CH2CH3 >O-CH3CH3

3-aminopropyltriethoxysilane

 $\sim CH_3$ $CI-CH_2CH_2CH_2CH_2Si - CI$ $\sim CH_3$

4-chlorobutyldimethylchlorosilane

Figure 5.2: Examples of two types of silane compounds, i.e., the ethoxysilanes and the chlorosilanes. In this work the first compound has been used for silica surface modification.

For the modification of surfaces one can choose between alkoxysilanes or chlorosilanes (figure 5.2). Furthermore, either mono-, di- or tri-substituted compounds can be used. Alkoxysilanes can be deposited from aqueous alcohol solutions or even from water (if the silane is soluble in water). Chlorosilanes are usually deposited from organic solvents. If larger amounts of water are present often bulk polymerisation occurs. $R-Si-X + H_2O \longrightarrow R-Si-OH + HX$



Figure 5.3: Coupling of silane layers to a surface. The first step is hydrolysis of the silane. In the second step the silane reacts with the surface silanol group (chlorosilanes, X = Cl, alkoxysilanes $X = Cn_{2n+1}O$).

In figure 5.3 the reaction of the silane compound with the surface is schematically shown. When di- or tri-substituted silanes are used, the silane cannot only couple to the surface but also to hydroxyl groups on other silane molecules. This can lead to crosslinking between the silanes coupled on the surface which enhances the stability of the layer. A self-assembled layer of silane is essentially a polysiloxane backbone cross-linked to the surface. This type of layer is typically less ordered than other types of SAMs [22].

5.2.3 Alkanethiol monolayers

On metals alkanethiols form self-assembled monolayers. Usually gold has been used as the substrate for two reasons: (1) gold has a strong specific interaction with sulphur (2) it was believed that gold does not have a stable oxide (recently however it was shown that such a stable oxide does exist [23]). During the adsorption a covalent gold-sulphur bond is formed. The best SAMs are obtained using long-chain alkanethiols $HS(CH_2)_n R$ with n > 10. The outer properties of these monolayers are practically independent of the chain length once this is larger than 10 [24, 25]. The adsorption is usually done from an organic solvent such as ethanol. After adsorption a densely packed and highly ordered monolayer is formed which has a nearly crystalline structure. The alkyl chains are stretched and the molecules are tilted by about 25 to 30 degrees with respect to the normal on the surface [22]. The strong specific interaction of sulphur with gold makes it possible to incorporate various chemical end groups (-R) without disturbing the binding to the gold surface. Using a simple alkanethiol with a terminal methyl group ($R = CH_3$) results in a hydrophobic surface. Using an alkanethiol with R = OH or with R = COOH gives hydrophilic surfaces. In this work a thiol with a carboxylic acid functional end group was used, namely 11-mercapto undecanoic acid.

Reaction of the alkanethiol with the gold surface leads to gold(I)thiolate which implies the loss of the S-H proton [26, 27]. The mechanism of the reaction is, however, not completely understood.

Two mechanisms have been proposed [28]:

1) $R(CH_2)_n$ -S-H + Au \rightarrow $R(CH_2)_n$ -S-Au + 1/2 H₂ 2) $R(CH_2)_n$ -S-H + Au + Oxidant \rightarrow $R(CH_2)_n$ -S-Au + 1/2 H₂O

This second mechanism requires the presence of (traces of) oxidant, for example, oxygen in the atmosphere or present in the liquid.

5.3 Monolayer preparation and characterisation

5.3.1 Amino-functionalised silane layers on silica

The silica particles and wafers used here came from the same batches as those used in the experiments described in chapter 3. The silica spheres were glued to AFM cantilevers before they were modified using silane chemistry.

The pretreatment of the surface is crucial for the coupling of the silane and for the final structure of the monolayer. To obtain a high density of Si-OH groups the silica wafers were cleaned by immersion in either hot (90° C) chromic acid or in a "piranha solution", *i.e.*, a hot mixture of 30% H₂O₂ and concentrated H₂SO₄, for 20 minutes. According to literature [29] this would lead to densities up to 5×10^{18} Si-OH groups per m². This concentration of OH groups is sufficient for binding the maximum possible number of alkyl chains per surface unit (assuming a lateral packing density of 0.20 nm² per molecule [30, 31]). The water/air contact angle of the silica wafers after cleaning was zero ($\theta_{water} = 0^{\circ}$). Silica particles on the cantilevers were cleaned for 10 minutes in moderately hot (50-60°C) chromic acid. This procedure did not damage the cantilever, as was checked by optical microscopy.

The obtain a surface with amine terminal groups silica was modified using 3-aminopropyl-triethoxysilane $H_2N(CH_2)_3Si(OC_2H_5)_3$ purchased from Petrarch (United Chemical Technologies, USA; cat.nr. A750).

As pointed out in section 5.2.2 water is required in the first step of surface modification with ethoxy silanes, the hydrolysis to silanol. Typically, a concentration of 5 mM ethoxy silane in a solution of 95/5 v/v ethanol/water is used. However, because the glue used to attach the particles to the cantilever is soluble in ethanol, in

our procedure the modification was done from pure water. This poses no problem as the aminosilane used here readily dissolves in water at room temperature. Since the abundance of water might promote bulk polymerisation, the silane solution was always prepared freshly. The silane was dissolved in NANOpure water and the solution was stirred for five minutes to allow hydrolysis and silanol formation to occur. The freshly cleaned silica surfaces were then immersed in the solution for approximately 20 minutes after which they were thoroughly rinsed in water and dried in a stream of nitrogen. The surfaces were annealed overnight at room temperature in dry atmosphere.

5.3.2 Carboxylic-functionalised thiol monolayers on gold

Gold-coated surfaces for AFM force experiments were obtained by sequential vacuum deposition of (1) a thin layer (5 nm) of titanium and (2) a somewhat thicker (15 nm) layer of gold onto silica particles and oxidised silicon wafers. The titanium layer serves to enhance the adhesion of the gold layer to the silica support. The silica particles and wafers were again from the same batches as those used in the experiments described in chapter 3. As described in section 3.2 the silica spheres were gold-coated *after* they had been glued to AFM cantilevers. The flat gold surface was cleaned by immersion into a piranha solution for 2 minutes [28]. This results in a surface with a zero contact angle with water. To avoid damage to the cantilever the gold-coated particles were not cleaned in piranha solution, but in a plasma cleaner (model pdc-32G, Harrick Scientific, New York, USA).

Gold surfaces used in streaming potential measurements were prepared by coating microscope glass slides with a titanium-gold layer following the same procedure as used for coating the silica wafers and particles. Cleaning was done in the same way as used for the gold-coated silica wafers.

Immediately after cleaning, the gold surfaces were immersed in a freshly prepared solution of 3 mM *11-mercapto undecanoic acid* HS-(CH_2)₁₁-COOH (obtained from Aldrich) in ethanol p.a. After 3 hours of incubation at room temperature the samples were thoroughly rinsed with ethanol and dried in a stream of nitrogen.

5.3.3 Contact angle measurements

To asses the quality of the self-assembled silane and thiol layers and to check whether the surface contains functional groups, the contact angle with water was measured as a function of pH. The surface free energy and, hence, the contact angle on the functionalised surfaces depends on the ionisation state of the functional groups. It is expected that the change of the contact angle with pH is largest in the pH range around the pK of the surface functional groups. Obviously, a change in the contact angle can

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only be measured if the surface is not completely hydrophilic at all ionisation states of the surface bound groups.

Contact angles on the flat substrates were measured using a Krüss contact angle meter G1 (Krüss GmBH, Germany). No attempt was made to determine the contact angle on the colloidal probes. The substrates used in the force experiments were always new (unused) surfaces, prepared following the same experimental procedure as for the substrates on which contact angle experiments were performed.



Figure 5.4: Advancing (circles) and receding (squares) contact angles of water on an aminefunctionalised silica surface $(I=10^{-2} M)$. Note the double ordinate axis; the advancing contact angle corresponds to the left ordinate axis and the receding contact angle to the right ordinate axis.

Creating amine-functionalised layers using silane chemistry results into rather hydrophobic surfaces. For such a layer the contact angle was determined as a function of pH. The results are shown in figure 5.4. The total ionic strength of the water was 10^{-2} M at all pH values, adjusted using NaCl.

From figure 5.4 we see that with increasing pH both the advancing and the receding contact angle increase. The change in the contact angle is caused by deprotonation of the surface group. Since in this graph the largest change in contact angle is found around pH 5 we conclude that for the surface-bound amine groups the apparent pK is about 5. This is considerably lower than for comparable amines in bulk solution. The pK of amine groups in aqueous solution is around 10 (for example, for *n*-butylamine pK = 10.8 [32]). The shift is, however, not unexpected: actual pK values for basic chemical groups on SAM surfaces are usually 3 - 5 units of pH lower as compared to

pK values in solution [33]. Significant differences with respect to the solution pK have been found in particular for surface-bound amine groups that are poorly solvated [34] or when the groups are in a somewhat hydrophobic environment [33].

Although the general trend with pH is the same, the advancing and receding contact angle show a strong hysteresis. This phenomenon has been reported also for other amine-functionalised surfaces. e.g., for heptylamine monolayers by Chatelier et al. [34]. These authors point out that the usually invoked reasons for hysteresis in contact angle measurements, i.e., surface roughness and chemical heterogeneity, are not sufficient to explain the strong hysteresis found for these layers. We suggest that the cause probably lies in reorientation of the surface amine as follows. While measuring the receding contact angle the determining part of the monolaver is in contact with water. The amine groups prefer to be oriented towards the water and this results into a hydrophilic surface with a low contact angle. However, when measuring the advancing contact angle the determining part of the monolaver is in contact with air and part of the amine groups is oriented towards any remaining hydroxyl groups on the silica surface. As a result the outside of the monolaver contains a larger fraction of -CH₂- groups, effectively rendering the surface more hydrophobic. This explanation only holds if in the monolayer there is still room for reorientation which could indicate that the density of amine groups is lower than expected.

Carboxylic layers on gold are hydrophilic over the entire pH range with contact angles below 2°. In this case measuring the contact angle as a function of pH yields no extra information. The contact angle was therefore only measured to check that the surface was hydrophilic and free of contaminants.

5.3.4 Streaming potential measurements

Generally it is found that the stability of self-assembled silane layers in organic media is very good [28]. However, in aqueous solution the stability of such layers seems to be more questionable [10]. Therefore, we studied the stability of the self-assembled monolayer using streaming potential measurements. For the aminosilane layers these measurements were performed in KCl solutions, and as a function of time. To determine the influence of the pretreatment of the silica surface on the number of functional groups and on the stability of the layer, three aminosilane layers were prepared on silica pretreated with concentrated chromic acid, HCl (0.1 M), and NaOH (0.1 M), respectively. The streaming potential measurements were performed in the way described in chapter 3. The zeta-potentials were calculated using the Helmholtz-Smoluchovski equation (equation 3.22).



Figure 5.5: Zeta-potential of silica surfaces modified with 3-amino-propyltriethoxysilane in 10^3 M KCl at pH 6. a) Silica surface pre-treated with concentrated chromic acid, b) with 0.1 M HCl, and c) with 0.1 M NaOH.

In figure 5.5 the zeta potential of the amine layers is given as a function of time. As the zeta-potential of the chromic acid pretreated surface is the most positive, we conclude that on this surface the density of amine groups is the highest. It is clear that over long periods of time the layers are not stable in aqueous solution. There is a steady and ongoing loss of surface groups and the initially positively charged surface even becomes negatively charged at a certain point. After a few days the surface has about the same zeta-potential as a bare silica surface (-50 mV) indicating that the entire aminosilane layer is then lost in solution. At pH 3 ($I = 10^{-3}$ M) the degradation of the layer proceeds about two times faster (results not shown). We expect that at very low pH (pH < 2) the layer will be highly unstable due to the hydrolysis of the Si-O bond (this has not been checked). From figure 5.5 it seems that the rate of degradation is constant over a long period of time and rather independent of the pretreatment. These observations demonstrate that the silane layer is not suitable for long-time use in aqueous environment. Storing silane-modified surfaces should therefore not be done in aqueous environment. When the layer is only used for a smaller time span (<3 hours) the layer can be considered to be relatively stable.

The stability of the thiol layer on gold was also studied by streaming potential measurements. The zeta-potential was followed in time and the results are presented in figure 5.6.



Figure 5.6: Zeta-potential of gold surfaces modified with 11-mercapto undecanoic acid in 10^3 M KCl measured as a function of time.

The zeta-potential is much more negative than the zeta-potential of the bare gold surface at neutral pH (-18 mV; see section 3.3). This confirms that carboxylic groups are present on the gold surface. In time the zeta-potential slowly becomes less negative, showing that the thiol layers are not completely stable in aqueous solution either. However, the rate of degradation is far slower than for silane layers on silica. After 50 hours the zeta-potential is still very much different from the zeta-potential of the bare gold surface. This indicates that a significant number of surface carboxyl groups remains.

5.4 Force measurements

5.4.1 Experimental

In the force measurements freshly prepared amine and carboxylic acid functionalised surfaces were used, as described in sections 5.3.1 and 5.3.2. The force measurements were performed as in the previous chapters. For experimental details the reader is referred to section 3.3.

5.4.2 Results and discussion

Amine-functionalised surfaces

The interaction between two amine-terminated layers was investigated in aqueous

solutions in the pH range 2 - 11 at two ionic strengths: $I = 10^{-2}$ and 10^{-3} M. Force curves measured on approach at pH 3, 5 and 8 are presented in figure 5.7.

At low pH (\leq 3) the force curves on approach and on retraction are identical and completely repulsive. The force decays exponentially with distance, which suggests that the repulsion is of an electrostatic nature resulting from the positive charge of the amine groups at this low pH. When the pH of the solution is increased the repulsion on approach gradually changes into an attraction as illustrated in the middle diagram of figure 5.7. Above pH 8 the attraction on approach is lost and only a small repulsion at short distances remains (not plotted). The attraction on approach found in the intermediate pH range seems puzzling since the surfaces are supposed to be of equal charge sign, the amine layers being partly protonated. It should be noted, however, that the monolayer on the colloidal probe may differ from the monolayer on the flat surface. The colloidal silica probe has been cleaned in a milder way before silanisation than the silica wafer and therefore the amine group densities and the charge densities at the two surfaces may be (significantly) different (see figure 5.5). As we have seen in chapter 3, dissimilar surfaces of the same charge sign can attract each other if they do not maintain constant charge on approach. As an illustration in the middle diagram of figure 5.7 interaction curves calculated using the Poisson-Boltzmann equation for dissimilar surfaces are given. Although we have tried to get the experimental approach curves in between the calculated curves for the limiting cases of constant potential and constant charge, these curves are not best fits to the data but mere examples. As pointed out in chapter 3, for dissimilar surfaces fitting the data is not possible without knowledge of the degree of surface charge regulation and of at least one of the two potentials at infinite separation. Nevertheless, the calculated curves show that the observed force curves at different pH values can be adequately explained as resulting from electrostatic interactions. No Van der Waals interaction is measured as can best be seen from the first plot of figure 5.7. As the ratio of the surface potentials becomes more extreme the interaction between the surfaces changes from repulsive into attractive

At most pH values (pH > 3) the force curves on separating the surfaces are different from those measured upon approach and an adhesive force is measured upon retraction. The magnitude of this adhesion was determined in the same way as described in chapter 4 and is plotted in figure 5.8 as a function of pH. In general the adhesion can be the result of interactions in the contact area (*e.g.* acid-base interactions, hydrogen bonding) and interactions outside the contact area (electrostatic interaction).



Figure 5.7: The interaction force on approach between amine terminated silica surfaces at three pH values ($I = 10^{-3}$ M). The symbols represent the experimental data. The curves are Poisson-Boltzmann calculations for constant charge (dashed curves) and constant potential (solid curves) for asymmetric surfaces. Potentials at infinite separation used in the calculations: pH 3 - 60 mV (plate) 30 mV (probe); pH 5 - 50 mV (plate) 18 mV (probe); pH 8 - 40 mV (plate) 2 mV (probe).



Figure 5.8: Adhesion force measured upon separation of the amine surfaces determined in the pH range of 2 - 11.

We attribute the adhesion to hydrogen bonding between protonated and deprotonated surface groups. At low pH all surface groups are protonated and no H-bonding occurs,

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there is only electrostatic repulsion between positively charged surfaces. When the pH increases part of the amine groups is deprotonated and hydrogen bonding can occur between NH_2 and NH_3^+ groups. On the basis of this one would expect a maximum in adhesion at pH \approx pK, *i.e.*, when circa 50% of the amine groups is protonated. However, the maximum in adhesion in figure 5.8 lies around pH 8 whereas the results from the contact angle measurements suggest a pK value of about 5 (figure 5.4). This deviation may be explained by additional hydrogen bonds between NH_2 groups and any remaining (unreacted) surface silanol groups. Above pH 8 the adhesion force sharply drops to zero, when all surface groups, silanol as well as amine, are in their deprotonated form. Using chemical force microscopy Noy *et al.* [35] have found similar results for the adhesion between amine terminated layers in the pH range up to pH 8. However, in their study the adhesion reaches a plateau value at pH 8 and does not decrease any more in the pH range studied (up to pH 11).

From figure 5.8 we see a strong effect of the ionic strength on the adhesion force. At 10^{-2} M the measured adhesion is much smaller than at 10^{-3} M. Since the strength of individual H-bonds does not significantly depend on electrolyte concentration, it is concluded that either the number of H-bonds decreases with electrolyte concentration (screening of binding sites, counter ion complexation), or that a considerable part of the adhesion is due to electrostatic attraction (as seen on approach) between the parts of the surfaces directly adjacent to the areas of real physical contact.

Carboxylic acid-terminated monolayers

The interactions between carboxylic acid layers were also studied as a function of pH, in the range between pH 2 and pH 11 and at two ionic strengths, 10^{-3} and 10^{-2} M. In figure 5.9 approach curves at different pH values and I = 10^{-3} M are given. At high pH values the interaction on approach and on retraction is identical and purely repulsive.

This repulsion can be attributed to the fact that at high pH the carboxyl groups are negatively charged $(-COO^{-})$.



Figure 5.9: The interaction force between carboxylic acid terminated gold surfaces on approach at three pH values ($I = 10^{-3}$ M). The electrostatic repulsion at pH 11 is fitted using the Poisson-Boltzmann equation for constant charge (dashed curve) and constant potential (solid curve). From this fit a surface potential at infinite separation of -60 mV was found.

The interaction curves for pH values in the range 8 to 11 are practically identical, indicating that above pH 8 all carboxyl groups are deprotonated and the surface charge and potential are almost constant. From a Poisson-Boltzmann fit the surface potential at pH 11 was determined to be -60 mV. At lowering the pH the repulsion on approach gradually changes into an attraction (see figure 5.9). As was found with amine layers an attraction is found in the intermediate pH-range (4 - 7). The attraction may again be electrostatic in nature, resulting from differences in surface charge densities or potentials between the colloidal probe and the flat surface. It should be noted that the interaction curves are not as nice as usually found. The interaction unsteadily goes up and down (0 < 10 nm). This makes it rather difficult to accurately identify the constant compliance region and to determine the exact distance between the surfaces. The trend of the interaction with pH, however, is still quite clear and remarkably similar as was found for the amine layer with, obviously a reverse scale for the pH.

Below pH 8 an adhesion is measured when the surfaces are separated (see figure 5.10). The magnitude of the adhesion increases when the pH of the solution is lowered. As for the amine functionalised surfaces the adhesion may result from hydrogen bonding between protonated and unprotonated surfaces groups. At high pH the charged groups (-COO⁻ repel each other and no hydrogen bonding is possible. As the pH of the solution is lowered, more and more carboxyl groups become uncharged, the repulsion between the surfaces decreases, and hydrogen bonding between the

groups becomes possible. As found for the amine surfaces the adhesion is less for higher ionic strength of the solution.

The maximum adhesion is expected when all carboxylic groups are protonated. The largest change in the adhesion occurs around pH 5 (at 10^{-3} M). From this the pK of the surface carboxyl groups is estimated to be approximately 5. This is very close to the values normally found for carboxylic acids with simple alkyl chains in aqueous solution (*e.g.* acetic acid CH₃COOH with pK = 4.76, proprionic acid CH₃CH₂COOH with pK = 4.89) and in line with what has been reported in literature [33, 36].



Figure 5.10: Adhesion measured upon separation of the carboxyl functionalised surfaces.

Interactions between amine and carboxylic acid-terminated monolayers

The interaction between a gold-coated surface modified with a carboxylic acid terminated layer and a silica sphere modified with an amine terminated layer was determined in the pH range 3 - 11, again in solutions of ionic strength 10^{-3} M and 10^{-2} M. Figure 5.11 shows the approach curves for a number of pH values in 10^{-3} M solutions.



Figure 5.11: The interaction on approach between an amine terminated layer on silica and a carboxylic acid terminated layer on gold in 10^3 M solutions at number of pH values.

At pH 6 and 7 the layers have opposite charge signs, which results in an attraction. Note the typical shape of the curves which results from a quick "snap-in" to the surface. This jump happens when the attraction exceeds the maximum attractive force measurable by the cantilever.

At high pH we have a charged and an uncharged surface (amine groups uncharged and carboxyl groups charged at pH > 9) and this is also the case at low pH (carboxyl groups uncharged and amine groups charged at pH<3). We find in both cases

repulsion between the charged and the uncharged surface. The interaction between the two is in fact compression of a single double layer and corresponds to an interaction close to the constant charge case (see fig 5.12).



Figure 5.12: The interaction between a charged and an uncharged surface (pH 9).

At pH 4, the amine surface is positively charged and the carboxylic surface is only slightly (negatively) charged. At distances larger than 20 to 30 nm a repulsion between the surfaces is observed. This repulsion probably stems from compression of the amine double layer. At closer distance the charge difference between the surfaces begins to play a role, and the interaction changes from repulsive to attractive. Apparently some degree of charge regulation occurs. A smaller but similar effect can be seen at pH 3, as shown in the discontinuity in the approach curve. This effect is not observed at high pH when the carboxylic acid layer is charged and the amine layers is uncharged.

On separating the NH_2 and COOH functionalised surfaces an adhesion is measured. The adhesion force as a function of pH at two ionic strengths is plotted in figure 5.13. The trend of the adhesion with pH is in line with that of the electrostatic interaction on approach. Because the surfaces are now in contact, acid-base interactions are likely to play a role in the adhesion. However, this is not the only contribution as can be concluded from the strong dependency of the adhesion on the ionic strength, especially in the intermediate pH range. This points to an electrostatic contribution, resulting from attraction between the oppositely charged surfaces, especially just outside the actual contact area where they are still very close.

It is to be expected that surface roughness plays a role in the effect of the ionic strength on the adhesion: surface roughness reduces the real physical contact area, but

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- on the other hand - leads to an increase in the area where the surfaces are very close (*i.e.*, just not touching), leading to a large overlap of their double layers and therefore to a large effect of dissolved ions on the interaction.



Figure 5.13: Adhesion force measured upon separating the amine surface from the carboxylic surface.

Adhesion forces

In a number of studies [36-40] the adhesion, or pull-off, force determined with AFM is evaluated using the Johnson, Kendall and Roberts (JKR) approach [41]. In this theory it is assumed that in the zone of contact between a spherical object and a flat surface a deformation develops spontaneously, depending on the interfacial interaction and any external load applied. The JKR relationship predicts the force required to pull a sphere (radius R) from a plate:

$$F_{adh} = \frac{3}{2} \pi R W \quad (JKR) \tag{5.1}$$

where W is the work of adhesion. Note that neither the elasticity of the substrates nor the contact area appear in this equation. The JKR approach has been developed for
relatively high adhesive forces and soft materials. For hard surfaces and low adhesion the Derjaguin, Muller and Toporov (DMT) theory [42] is a better approximation. However, the choice of approach to calculate the work of adhesion from the pull-off force is not crucial, since the equation given by the DMT theory differs only a factor of 4/3 from the JKR relationship:

$$F_{adh} = 2\pi R W \quad (DMT) \tag{5.2}$$

This is essentially the Derjaguin equation (equation 2.7) applied to the pull-off point. Using this equation we calculated the work of adhesion from the experimentally determined pull-off forces. The results are given in table 5.1.

Table 5.1: pH at which maximum adhesion occurs and corresponding work of adhesion W_{max} calculated from the pull-off forces F_{adh} (at $I = 10^{-3}$ M) using the DMT theory

interaction	pHmax	F _{adh}	W _{max}
		(nN)	(mJ m ⁻²)
NH ₂ -NH ₂	~ 8	21.2	1.13
COOH-COOH	≤4	10.9	0.58
NH ₂ -COOH	~ 7	30	1.59

The largest adhesion is found between an NH_2 - and a COOH-functionalised surface; the adhesion between two NH_2 layers is relatively strong as compared to the adhesion between two COOH surfaces. This is in line with the scarce literature data available.

According to the Dupré equation [43] the reversible work of adhesion, that is the free energy change per unit area in creating an interface between two bodies, equals

$$W = \gamma_1 + \gamma_2 - \gamma_{12} \tag{5.3}$$

with γ_1 and γ_2 the surface free energies of each of the surfaces in contact with the medium, and γ_{12} the interfacial free energy of the surfaces in contact

For identical surfaces $\gamma_1 = \gamma_2$ and $\gamma_{12} = 0$, so that the work of adhesion (cohesion) becomes

$$W = 2\gamma_1 \tag{5.4}$$

Values reported in literature for the work of adhesion between functionalised surfaces in aqueous solutions and related quantities are still scarce and vary substantially. Furthermore, the systems investigated are not always comparable to the systems studied here. However, it is clear that the values found here for the work of adhesion are low compared to literature. For example,

- Tsukruk and Bliznyuk [44] report a maximum work of adhesion between two NH₂ - terminated layers of 4.5 mJ m⁻² (at pH 4.0 – 4.5), measured using colloidal probe AFM and calculated using the JKR relationship.

- Both Vezenov *et al.* [45] and Clear *et al.* [37] report a surface free energy for fully protonated COOH surfaces in water of ca 16 mJ m⁻² determined by AFM using chemically modified tips, from which a work of adhesion of 32 mJ m⁻² follows for COOH-COOH interaction.

- According to Thomas *et al.* [46] the work of adhesion for NH₂-NH₂ amounts to ca 100 mJ m⁻², for COOH-COOH to 230 mJ m⁻² and for NH₂-COOH to 680 mJ m⁻². These results were obtained using interfacial force microscopy (using a self-balancing force-feedback to avoid the mechanical instability encountered in AFM) to measure the interaction between SAMs on a gold substrate and a gold tip in aqueous solutions. These values, however, seem to be much too high, considering that the absolute values of surface energies for different surfaces in water are substantially (several times) lower than the solid-vapor surface energies, known to be in the range of 20 mJ m⁻² (CH₃ SAMs) to 50 mJ m⁻² (NH₂ SAMs) [44]. The surface free energy for long-chained carboxylic acid SAMs in water is usually found to be 10 - 11 mJ m⁻² [47].

- The adhesive forces reported by Van der Vegte and Hadziioannou [36] also appear to be (too) high. They have found maximum adhesive forces of 14 nN for NH_2-NH_2 and 9 nN for COOH-COOH interactions in water, measured between n-alkanethiol SAMs on gold-coated AFM tips and flat surfaces. Although the effective radius of the tips (ca 35 nm) is much smaller than that of our colloidal probes, these forces are of the same order as the adhesive forces measured in our study (see table 5.1). It implies that the corresponding work of adhesion for would be of the order of 100 mJ m⁻².

Equations 5.3 and 5.4 are derived for physically ideal (*i.e.*, smooth) interfaces. Adhesion is known to be dramatically reduced due to the roughness of component surfaces, because the real contact area is reduced [48]. This may explain the relatively low value for W found in this work. Probably, the effect of surface roughness is less when a chemically modified AFM tip instead of a micrometer-sized particle is used to measure adhesion forces. On the other hand, the force resolution and reproducibility of the measurements will also be much less, making it necessary to conduct and average a large number of adhesion force measurements. Furthermore, the tip geometry and radius are not well-defined and vary from tip to tip.

From the calculated work of adhesion the number of molecular contacts can be calculated, provided that the individual bond strength is known. Alternatively, the bond strength may be obtained if the number density of groups at the surfaces and the actual contact area is known. In the JKR theory the radius of the contact area at pull-off, a, is given by

$$a = (3\pi W R^2 / K)^{1/3}$$
(5.5)

where K is the effective elasticity modulus of the surfaces. A problem is that generally K is not known. Often the elasticity modulus of the substrate material is taken and that of the surface layer is ignored (e.g., refs [36,37]).

From our results we can roughly estimate the density of molecular contacts between the interacting surfaces. Assuming that the free energy change for disrupting the NH₂-COOH acid-base bonds in water amounts to 40 kJ mole⁻¹, W = 1.6 mJ m⁻² corresponds to the breaking of about 2.4 x 10¹⁶ NH₂-COOH contacts per m². Since for a complete COOH-terminated thiol SAM the maximum density of COOH groups is about 5 x 10¹⁸ m⁻², this would imply that only about 0.5 % of the surface groups is involved in the adhesion. Probably due to surface roughness only a fraction of the surface groups is involved in the interaction or the surface layers are rather incomplete, especially of the NH₂-silane layer. Most likely both factors play a role in this.

Calculation of the radius of the contact area according to the JKR theory (equation 5.5), using an elasticity modulus of 64 GPa (the bulk value of gold [38]), a the colloidal probe radius of 3 μ m, and a work of adhesion W = 2.12 mJ m⁻² (the JKR value for NH₂-COOH interaction at pH 7), gives 1.4 x 10⁻⁸ m. The corresponding contact area is 2 x 10⁻¹⁶ m², in which area about 1000 pairs of surface groups would be found (assuming complete monolayers).

5.5 Conclusions

In this chapter we presented an AFM force study on interactions between chemically modified surfaces. Surfaces with terminal groups of either NH₂ or COOH were obtained by chemisorption of a silane-based compound on silica or a thiol compound on gold, respectively. The modified surfaces were characterised by means of streaming potential and contact angle measurements. For the NH₂-surfaces it was found that the density of functional groups strongly depends on the pretreatment of the silica surface. Probably, the surface modification of silica does not lead to homogeneous densepacked layers. Furthermore, the layers are not stable over long time periods (> 3 hours). The COOH-layers on gold are much more stable and show little degradation in time.

Colloidal probe force measurements between the various combinations of functionalised surfaces in aqueous solutions show a strong correlation with the state of ionisation (acid-base properties) of the surface groups. The approach curves can be explained completely on the basis of electrostatic interactions only, assuming that the charge density of a NH_2 or a COOH layer on the colloidal probe differs from the corresponding layer on the flat surface. Since the pretreatment before modification is different for probe and flat surface, this is a reasonable assumption. As before (see chapter 3), no evidence was found for Van der Waals forces.

On retraction a pH dependent adhesion was found, the strongest between NH_2 and COOH surfaces. This is attributed to acid-base interactions. Between NH_2 layers and between COOH layers there is also adhesion, due to the formation of H-bonds (between NH_2 - and NH_3^+ -groups and between COOH-groups, respectively). Since the adhesive forces do not only depend on pH but also on ionic strength, there must be a contribution of electrostatic interactions as well.

From the adhesion forces, the corresponding work of adhesion W was calculated using the DMT (Derjaguin, Muller, Toporov) equation. The values of W obtained are small compared to literature data and suggest that only a small fraction of the functional groups in the contact area is involved in acid-base or H-bond interactions. Probably this is due to surface roughness, which reduces the real contact area. At the same time, the surface roughness may cause the relatively strong dependence of the adhesion on the ionic strength, since it leads to a increase in the area were the surfaces are very close, *i.e.*, just not touching.

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Summary

Forces between surfaces are a determining factor for the performance of natural as well as synthetic colloidal systems, and play a crucial role in industrial production processes. Measuring these forces is a scientific and experimental challenge and over the years several techniques have been developed to measure the interaction between surfaces directly as a function of their separation distance. *Colloidal probe atomic force microscopy (colloidal probe AFM)* offers the possibility to study such forces between virtually all kinds of surfaces. Furthermore, the time scale of the measurements can be short enough to monitor relaxation effects and to study the interaction at *Brownian-like* collision rates. Combining this with the original application of the AFM, namely the imaging of surfaces at nanometer resolution, makes the AFM a versatile instrument in surface science.

The aim of the project at the basis of this thesis was twofold. In the first place it comprised implementation of colloidal probe AFM as an operational surface force measurement technique in the laboratory. Secondly, the aim was to study the forces that play a role in colloidal systems, especially with respect to the role of surface groups and polymer layers.

An introduction to forces acting between (colloidal) surfaces is given in chapter one. In addition, this chapter presents a short overview of the development and various applications of the atomic force microscope, especially with respect to its application as a surface force apparatus. In colloidal probe AFM a micrometer-sized particle (the colloidal probe) is glued to the end of an AFM cantilever and is moved towards and from a flat surface with the use of a piezo element. The deflection of the cantilever is measured as a function of piezo position and reflects the forces acting between the surfaces. The chapter concludes with an overview of the various techniques to directly measure surface forces. A comparison of three of these techniques, *i.e.*, the surface force apparatus (SFA), colloidal probe AFM, and a relatively new technique called MASIF (which stands for 'measurement and analysis of surface interaction and forces') is made. The most important advantages of colloidal probe AFM are (1) it can be applied to virtually any kind of interacting surfaces (the SFA, for example, is limited to transparant surfaces which are smooth over a relatively large area), (2) AFM force measurements are relatively easy to perform (a bit more difficult is glueing a particle onto a cantilever and calibration of the cantilever), and (3) measurements can be performed at speeds much higher than in the SFA. The most important disadvantage

Summary

of AFM force measurements is that there is no independent way to determine the distance between the surfaces; instead, this is derived from the raw deflection-piezo position data, the zero being identified from the region of constant compliance, where cantilever and piezo movements are coupled. This can be a problem when dealing with soft surfaces or surfaces covered with a compressible (adsorption) layer.

In *chapter two* the experimental ins and outs of the colloidal probe technique are described in detail. The chapter deals with topics such as colloidal probe preparation, cantilever calibration and conversion of the raw data into force-distance curves.

Chapter three presents colloidal probe force measurements on a silica-silica system in aqueous solutions of varying pH and electrolyte concentration. The results are compared to similar measurements by other authors and were found to be in good agreement with these earlier experiments, which confirmed the proper working of our surface force technique. The experimental data were fitted to the DLVO (Derjaguin, Landau, Verwey and Overbeek) theory. No indication whatsoever was found for Van der Waals interaction, which is in itself surprising but is in line with what is generally reported in literature. Most probably the Van der Waals interaction is obscured by non-DLVO short-range interactions, in particular hydration forces, and by surface roughness effects.

In the same chapter the interaction between gold-coated surfaces as a function of pH is described. For comparison, streaming potential measurements were performed as well. The zeta-potentials thus obtained for the gold-coated surfaces are in good agreement with the surface potentials derived from the gold-gold force measurements through Poisson-Boltzmann fits. As for the silica-silica systems, we found no evidence for a contribution of Van der Waals forces to the interaction. Of course, also in the gold-gold system the Van der Waals interactions may be partly hidden due to surface roughness or the presence of hydration layers. However, because of the high literature value for the Hamaker constant of gold, a significant contribution of the Van der Waals interaction was expected at distances up to 10 - 20 nm (!). The only possible conclusion is that the high Hamaker constant for bulk gold is not applicable for the systems studied, but the reason is not clear at all.

Finally, we studied the interaction between silica and gold surfaces. Overall, the results are in agreement with expectation. Above the iso-electric point (i.e.p.) of the gold surface ($pH \sim 4.5$) both of the interacting surfaces are negatively charged resulting in electrostatic repulsion. At low pH (pH 3, between the i.e.p.'s of the surfaces) the silica

and the gold have opposite charge signs and an attractive interaction is found. All experimental force curves are well in between the calculated Poisson-Boltzmann limits for two surfaces maintaining either constant charge or constant potential. In the case of dissimilar surfaces it is not possible to determine the potential of one of the surfaces from the interaction curves without knowledge of the potential of the other surface and of the charge regulation mechanisms. Depending on the latter, the interaction on approach between surfaces of opposite charge sign may change from attraction into repulsion, or repulsion between surfaces of the same charge sign may change into attraction. Indications of such phenomena was found for the gold-silica system around the i.e.p. of the gold surface, where the ratio between the surface charge densities is the most extreme.

In *chapter four* interaction forces are described between polymer-covered surfaces for different polymer chain lengths. The polymer used was poly(ethylene oxide) (PEO). The interaction on approach is dominated by electrostatic interaction. On separating the surfaces, however, a strong adhesion is observed, which is attributed to bridging. The adhesion shows a strong dependence on the chain length of the polymer. A linear relationship between the adhesion force and the surface coverage (*i.e.*, the adsorbed amount in mass per unit area) is found. However, adhesion occurs only for chain lengths above a certain threshold value. In order for this bridging to occur the surfaces have to be pressed together to some extent. At some pH values electrostatic repulsion inhibits this bridging and no adhesion is found. In these cases bridging can be induced by increasing the electrolyte concentration or increasing the load-force.

The topic of *chapter five* is interactions between acid- and base-functionalised surfaces. Silica and gold-coated silica surfaces were modified with self-assembled monolayers with amine terminal groups and carboxylic acid terminal groups, respectively. Especially for the NH₂ modified silica surfaces, we found that variations in the pretreatment of the surface results into differences in the density of functional surface groups. Probably, the surface modification of silica does not lead to homogeneous dense-packed layers. The interaction upon approach between the different combinations of surface layers can be explained from electrostatics, assuming that for the NH₂-NH₂ and COOH-COOH combinations the surface layers on the colloidal probe and the flat surface are not identical (due to differences in pretreatment of probe and flat surface). On approach the NH₂-NH₂ system and the COOH-COOH system show the same trends: repulsive when the surface layers carry a large charge, but as the pH changes in the direction where more surface groups become uncharged

the repulsion changes into an attraction. On retraction all combinations of modified surfaces show a pH dependent adhesion, the strongest between NH_2 and COOH surfaces. This is attributed to acid-base interaction (between -COO⁻ and - NH_3^+) and hydrogen bonding (between - NH_2 and - NH_3^+ and between -COOH and -COOH). As compared to literature data, the adhesion forces are low. Probably, the roughness of the surfaces, which reduces the real physical contact area, is the most important cause for this weak adhesion. Surface roughness may also lead to the large influence of the ionic strength on the adhesion force since a part of the adhesion force originates from electrostatic interaction especially just outside the actual contact area.

Epilogue

DLVO theory

Development of AFM into a surface force technique has made it possible to measure surface forces between a wide range of substrates. From the work described in this thesis and from literature it is obvious, however, that the *interpretation* of the measured force curves is still far from straightforward. For many systems the DLVO theory does not give an adequate description. For example, we have found no indication whatsoever for a Van der Waals contribution in the interaction curves for the systems studied here, and even 'simple' electrostatic interactions between similar surfaces become complicated to predict when the surfaces are not completely identical.

In literature a whole range of non-DLVO interactions is used to explain deviations from DLVO theory. Incorporating all these effects in existing theory to calculate net interaction forces is an enormous task and probably not very useful until there is more clarity. In particular, there is a gap between theory, which usually assumes sharp, homogeneous and smooth interfaces and experiment that is confronted with real, nonideal and often rough surfaces. As a result theories developed to describe the interaction between surfaces can seldom strictly and quantitatively be applied to surfaces encountered in practice. Surface roughness may partly or completely obscure short-range interactions like Van der Waals forces, and it greatly affects adhesion due to reduction of the physical contact area. We asses that the most practical step in the near future is to investigate the role of surface roughness by systematic experiments and try to incorporate this in theory.

For electrostatic interaction between dissimilar surfaces even the sign of the interaction – attractive or repulsive – may vary, depending on the charge regulation mechanism (constant charge, constant potential) and the ratio between the charge densities on the two surfaces. Using the Poisson-Boltzmann equation for dissimilar surfaces, a large variety of interaction curves can be obtained between the two limits of both surfaces either maintaining constant charge or constant potential. Therefore, whether or not the observed interaction is really electrostatic in nature cannot be checked by just fitting the data to DLVO with an optional Van der Waals interaction. To understand the behaviour of such systems one should carefully characterise both surfaces and preferably measure their interaction with various types of other surfaces, also well-characterised. The nature of the interactions may be further elucidated by varying solution parameters like electrolyte concentration, pH and polarity.

Epilogue

The most important aspect at present is that the AFM offers the possibility to perform measurements on all kind of different surfaces and to gain insight into the nature of the interactions between them. In that sense AFM is a very valuable surface force measuring technique of which the potentiality in the near future certainly will be extended.

Soft surfaces

In today's AFM there is no independent way to measure the zero of separation between the surfaces. This may be a problem when surfaces can be deformed (for example, in case of polymers, or surfaces of bubbles and vesicles). We expect that in the near future there will be technical solutions for this problem depending on the system to be studied (for example, interferometric measurement of the distance in case of the flat surface being transparant). Nevertheless, even if the absolute distance between soft surfaces is not exactly known, AFM force measurements can be very informative, although, obviously, care should be taken in the way of presenting and the interpretation of the results. By variation of the time scale of the approach and retraction cycle insight into the dynamics of the surface layers may be obtained.

New endeavours

In our department the rate of adsorption of surfactant, polyelectrolyte and protein molecules on a gold surface with externally controlled potential is studied. The advantage of this approach is that adsorption can be studied over a wide range of surface potentials without changing other experimental conditions, such as the substrate material and the composition of the solution. By AFM force measurements the surface potential with respect to the bulk solution can be determined by measuring the electrostatic force between the electrode and a spherical particle of which the surface potential is known.

Closely related to this is electro-deposition of particles onto surfaces. Deposition of colloidal particles from a liquid suspension is encountered in many industrial applications. An interesting application of the AFM would be to study electro-deposition by measuring the forces that work on a colloidal particle located in an electric field at different applied potentials and varying pH conditions. For this the relation between the surface potential and the applied potential needs to be investigated: (1) to what extend is the surface potential determined by the applied potential, and (2) how does the electrolyte conditions affect the (induced) surface

potential, e.g., by adsorption/desorption of potential determining ions or redox processes.

A new project at the department is aimed at studying the electric double layer and the elastic properties of lipid vesicles by AFM. An immobilised vesicle on a surface is probed using a colloidal particle to study the electric properties of the vesicles. Because the electric potential profile in and near biological membranes also has effect on the mechanical properties. AFM dynamic force modulation will be used to measure the elastic modulus of vesicles. In this technique an alternating modulation amplitude is applied to the AFM cantilever; interaction of the tip with the vesicle surface then results in changes in amplitude and phase shifts from which the (visco)elastic properties of the membrane can be derived.

Adhesion of biological cells to surfaces is an important topic in nature, medicine and industry. Bacterial adhesion, for example, could be studied by attaching bacteria to an AFM tip or to probe biofilms using a colloidal particle. In literature the AFM has already been used to measure the force of adhesion between a living yeast cell and a mica surface. These measurements can provide much information about the parameters that play a role in cell adhesion including the time scale of the development of the adhesive contact.

In conclusion, colloidal probe AFM can offer new experiments and insight into a range of systems in physical chemistry. The physical basis of colloidal probe AFM is now established. It is the opportunity of the inventive researcher to employ this and to explore new applications. With regards to the potential of the (colloidal probe) atomic force microscopy we have only scratched the surface.

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Samenvatting voor iedereen

Dit proefschrift gaat over krachten tussen vaste deeltjes in water. In het onderzoek beschreven in dit proefschrift zijn de krachten die werken tussen kolloïden en macroscopische oppervlakken gemeten met een Atomic Force Microscope (AFM). Als dit u allemaal niets zegt, lees dan vooral door. In deze (Nederlandse) samenvatting probeer ik uit te leggen wat kolloïden zijn en welke krachten een rol spelen bij kolloïden. Verder bespreek ik wat een AFM is en kunt u lezen waar de verschillende hoofdstukken in dit proefschrift over gaan. Mensen die meer geïnteresseerd zijn in een meer wetenschappelijke samenvatting verwijs ik naar de samenvatting in de Engelse taal.

Kolloïden

In de scheikunde kennen we oplossingen van stoffen in water. Sommige stoffen (zoals suiker of alcohol) lossen op als moleculen terwijl andere stoffen (zoals zouten) niet als neutrale moleculen oplossen maar uiteenvallen in ionen. Weer andere stoffen zoals goud, zilverchloride of zwavel lossen helemaal niet op in water. Onder bepaalde omstandigheden is het toch mogelijk om van deze slecht oplosbare stoffen (schijn)oplossingen te krijgen. In het water hebben we dan kleine klompjes goud of zwavel die bestaan uit vele (kleine) moleculen of atomen.

Deze deeltjes zijn vele malen groter dan eenvoudige moleculen en hun afmetingen liggen tussen enkele tientallen en honderden nanometers¹. Deeltjes van deze grootte noemen we kolloïden. Een kolloïdale oplossing is dus geen moleculaire oplossing. Omdat van zo'n deeltje het oppervlak in verhouding tot het volume erg groot is, spelen oppervlakte-eigenschappen een belangrijke rol in het gedrag van kolloïden.

Oplossingen van vaste deeltjes in een vloeistof, zoals de bovengenoemde goud- of zwavelkolloïden, noemen we *solen* of *suspensies*. Ook andere systemen vallen onder de noemer kolloïden. Het gaat hierbij steeds om de verdeling van één fase (vast, vloeibaar of gas) in een andere waarbij de 'deeltjes' van kolloïdale afmetingen zijn. Zowel de deeltjes als de fase waarin ze verdeeld zijn kunnen vast, vloeibaar of gasvormig zijn. Dus ook kleine druppeltjes olie in water (zoals in melk) zijn kolloïden.

Kolloïden komen we tegen op allerlei gebieden, in de natuur, in de chemie en in het dagelijks leven. Voorbeelden van eenvoudige kolloïden zijn de genoemde goud- en

¹ Zoals het voorvoegsel milli staat voor een duizendste deel, een millimeter is 0.001 meter, zo staat het voorvoegsel nano voor een miljardste deel. Een nanometer is dus 0.000000001 meter of 10⁻⁹ meter.

zwavelsolen, maar ook mist (vloeistof in gas), melk (vetdruppeltjes in water), rook (vaste stof in gas) en bierschuim (gas in vloeistof) zijn kolloïden.

Er zijn kolloïden die zich spontaan vormen wanneer je twee stoffen met elkaar mengt. Een voorbeeld van zo'n kolloïd is een zeepmicel in water. Micellen zijn aggregaten van zeepmoleculen. Een zeepmolecuul bestaat uit een deel dat graag in water oplost en een deel dat een vetachtige structuur heeft en daarom juist niet graag in contact is met water. Wanneer de zeepmoleculen in water worden opgelost dan zoeken de vetachtige delen van verschillende zeepmoleculen elkaar op. Het gevolg is dat er vele kolloïdale 'deeltjes' ontstaan die een vetachtige kern en een wateroplosbare buitenkant hebben. Micellen spelen een belangrijke rol in een wasproces, ze kunnen vuil (veelal vet) oppikken in de kern en zo oplosbaar maken in water.



figuur 1: Een zeepmolecuul (boven) met een 'staart' die weinig voor water voelt en een 'kop' die wel graag in water zit. De "grijsintensiteit" geeft de affiniteit voor water weer. In een micel (onder) heeft een aantal zeepmoleculen zich verzameld tot een (vloeibaar) bolletje in de vloeistof. De waterachtige delen zitten aan de buitenkant van de bol, de vetachtige delen zitten in het midden.

Andere kolloïden kunnen alleen door inspanning worden gemaakt en behouden. Wanneer je een stuk goud in water brengt, vormt zich daaruit niet spontaan kolloïdaal goud. Wel kun je goud vermalen tot deeltjes van de juiste grootte. Een andere manier is om goudatomen aan elkaar te laten groeien tot grotere kolloïdale deeltjes. Dit kan bijvoorbeeld door een wateroplosbare goudverbinding chemisch om te zetten in goud. Als je de omstandigheden goed kiest kunnen er uit deze atomen gouddeeltjes van de juiste afmetingen worden gevormd. In tegenstelling tot spontaan gevormde kolloïden zijn deze kolloïden van nature instabiel en zullen elke kans grijpen om uit de kolloïdale vorm te ontsnappen. Wanneer de deeltjes elkaar bij botsingen ontmoeten zullen ze in het geval van (netto) aantrekkende krachten aan elkaar blijven plakken en zo steeds grotere aggregaten vormen die uiteindelijk naar de bodem zakken. Het zal duidelijk zijn dat om een kolloïdaal systeem voor langere tijd te behouden (stabiel te houden) deze neiging tot samenklonteren (of uitvlokken, zoals men in de kolloïdkunde zegt) moet worden tegengegaan: er moeten afstotende krachten werkzaam zijn.

Krachten

Krachten spelen een belangrijke rol in kolloïdale systemen: in bovenstaand voorbeeld van een instabiel goudsol zagen we dat de door een *aantrekkingskracht* gevormde grote aggregaten onder invloed van de *zwaartekracht* naar de bodem zinken.

In eerste instantie zouden we ook verwachten dat de kleine kolloïdale deeltjes (waarvan de dichtheid veel hoger is dan van water) naar de bodem zakken. De zwaartekracht werkt tenslotte ook op kleine gouddeeltjes. Deze deeltjes zijn echter zo klein dat ze in de vloeistof blijven zweven doordat ze voortdurend botsen met de vloeistofmoleculen. Door deze botsingen bewegen de kolloïden zich wat chaotisch door de vloeistof. Deze chaotische dans heet de Brownse beweging¹. In dit voorbeeld werken dus al minstens drie krachten op de gouddeeltjes. Ten eerste de zwaartekracht (Sir Isaac Newton², 1687); ten tweede een temperatuursafhankelijke kracht ten gevolge van de Brownse beweging (Robert Brown, 1827) en natuurlijk de opwaartse kracht die de deeltjes ondervinden door de onderdompeling in water (Archimedes, 250 BC).

¹ Naar de ontdekker Robert Brown, een Schotse botanicus die in 1827 waarnam dat kleine stuifmeeldeeltjes in water onder de microscoop schijnbaar vanzelf een zigzag beweging maken.

² Volgens het welbekende verhaal zag Newton (rond 1666) in zijn boomgaard een appel vallen en realiseerde hij zich hierdoor dat het dezelfde kracht is (de zwaartekracht) die de beweging van de maan veroorzaakt en de appel doet vallen.

Samenvatting voor iedereen

Verder bestaan er aantrekkende en afstotende krachten. Er werkt altijd een aantrekkende kracht zoals *Van der Waals¹* heeft aangetoond. Deze krachten staan nu bekend als *Van der Waals-krachten*. Wat is nu de oorsprong van deze kracht? Een neutraal atoom bestaat uit een positieve kern en negatief geladen elektronen. Het is dan ook niet verrassend dat de elektronen van een atoom iets worden aangetrokken door de kern van een naburig atoom (gelijke ladingen stoten elkaar af en tegengestelde ladingen trekken elkaar aan). Dit is weergegeven in figuur 2. Vergeleken met de aantrekking van de elektronen met de eigen kern is dit effect klein maar niet te verwaarlozen.



figuur 2: De Van der Waals kracht tussen twee heliumatomen.

Bij kolloïden wordt dit effect versterkt doordat een kolloïddeeltje uit vele duizenden atomen bestaat en er dus vele Van der Waals wisselwerkingen tegelijkertijd plaats kunnen vinden. Het effect is echter alleen merkbaar op korte afstand. Dus alleen wanneer de deeltjes elkaar dicht genoeg kunnen naderen trekken ze elkaar door de Van der Waals kracht aan en vlokken uit.

Er zijn ook afstotende krachten tussen deeltjes die een kolloïdaal systeem juist kunnen stabiliseren. Een voorbeeld hiervan zijn de elektrostatische of Coulombse krachten² die bestaan tussen geladen oppervlakken. Gelijk geladen oppervlakken stoten elkaar af en tegengesteld geladen oppervlakken trekken elkaar aan. Geladen oppervlakken

¹ Johannes Diderik van der Waals, een Nederlandse natuurkundige die in 1910 de Nobelprijs voor natuurkunde kreeg.

² genoemd naar de Franse natuurkundige Charles Augustin de Coulomb

vinden we ook vaak bij kolloïden. Op kolloïden kunnen ionen geadsorbeerd zijn die het deeltje een oppervlaktelading geven. Doordat de (identieke) deeltjes allemaal dezelfde lading hebben, stoten ze elkaar af. De elektrische lading op de deeltjes houdt de deeltjes zo ver uit elkaar dat de Van der Waals aantrekking (die alleen op korte afstand werkt) geen rol speelt, en zorgt er zo voor dat ze niet kunnen aggregeren. De Coulombse kracht *stabiliseert* dan de kolloïden.

We zien dat om de krachten tussen twee kolloïdale deeltjes in oplossing te beschrijven we *in ieder geval* de ideeën van een oude Griekse wiskundige, een Franse natuurkundige, een Engelse wiskundige (onder een appelboom), een Schotse botanicus en een Nederlandse Nobelprijswinnaar nodig hebben.



figuur 3: Vijf wetenschappers en kolloïden, Archimedes - Griekse wiskundige (c. 287-212 BC), Isaac Newton - Engels natuur- en wiskundige (1642-1727); Robert Brown - Schotse botanicus (1773-1858); Charles Augustin de Coulomb - Franse natuurkundige (1736-1806).

Dit proefschrift

In dit proefschrift zijn de krachten die een rol spelen bij de stabiliteit van kolloïden gemeten m.b.v. een atomic force microscope, AFM (een microscoop die atomaire krachten meet). Een AFM is een nieuw type microscoop die een klein oppervlak heel erg vergroot op een computermonitor kan laten zien. De AFM brengt dit oppervlak in beeld door het met een scherp naaldje af te tasten (zie figuur 1.1 op blz. 6). Ongeveer zoals een platenspeler de groeven in een grammofoonplaat hoorbaar maakt, zo maakt de AFM de contouren van een oppervlak zichtbaar. Deze AFM kan omgebouwd worden tot een krachtmeetapparaat door op het naaldje een relatief groot kolloïdaal deeltje te lijmen. (zie figuur 2.2 op blz. 25). Dit is gedaan onder een gewone microscoop (d.w.z een lichtmicroscoop) met een speciale deeltjes-plak-opstelling. Bij zo'n krachtmeting wordt de naald met het deeltje naar een oppervlak toe bewogen en tijdens deze beweging wordt de kracht die er op werkt voortdurend gemeten. Het verloop van de kracht met de afstand tussen deeltje en oppervlak kan informatie geven over bijvoorbeeld hun lading.



figuur 4: Een krachtmeting in de AFM schematisch weergegeven.

In hoofdstuk één van dit proefschrift wordt een inleiding gegeven over de krachten die werkzaam zijn op kolloïden. Verder gaat dit hoofdstuk in op de toepassingen van de AFM, met name de toepassingen als krachtmeetapparaat. Het hoofdstuk sluit af met een overzicht van enkele andere technieken die gebruikt worden om krachten tussen oppervlakken te meten. De voor- en nadelen van deze technieken worden vergeleken met die van AFM. Het belangrijkste voordeel van AFM is dat je met deze techniek de krachten tussen vrijwel ieder type deeltje en ieder type oppervlak kan meten. Verder zijn de AFM metingen relatief eenvoudig uit te voeren en kun je ook *snel* meten. Het grootste nadeel van de AFM techniek is dat de afstand tussen de oppervlakken niet altijd precies bepaald kan worden.

In hoofdstuk twee worden de experimentele details van de techniek besproken. Er wordt onder andere uitgelegd hoe de deeltjes op de naald worden gelijmd en hoe je de krachten berekent uit de verkregen meetgegevens. In hoofdstuk drie worden metingen aan een silica (glas) deeltje en een silica oppervlak gepresenteerd. De resultaten worden vergeleken met metingen die door anderen gepubliceerd zijn en met berekeningen volgens theoretische modellen. De experimentele gegevens kwamen goed overeen met de metingen door anderen, wat bevestigde dat onze opstelling goed functioneert. Verrassenderwijs, maar in overeenstemming met metingen door anderen, zijn er geen aanwijzingen gevonden voor het optreden van Van der Waals krachten.

Waarschijnlijk blijft de Van der Waals kracht verborgen door de ruwheid van deeltje en oppervlak. Op de kortste naderingsafstand (bepaald door de grootste "uitsteeksels") is de Van der Waals kracht mogelijkerwijs nog steeds zo klein dat hij niet de ontdekken valt.

In hetzelfde hoofdstuk worden ook metingen aan een gouddeeltje en goudoppervlak behandeld. Net als bij silica vonden we geen Van der Waals krachten. Maar in het geval van goud-goud wisselwerking zou de kracht zo groot moeten zijn dat je hem toch wel opmerkt ondanks de oppervlakte ruwheid. Daar hebben we geen bevredigende verklaring voor.

Tenslotte zijn ook metingen uitgevoerd aan het systeem silicadeeltje en goudoppervlak. In alle gevallen bleken de wisselwerkingen sterk afhankelijk van de pH (= zuurgraad) van de oplossing. Dit komt doordat de oppervlaktelading van zowel goud als silica sterk afhangt van de pH. In neutrale of basische oplossing zijn zowel silica als goud negatief geladen wat voor afstoting zorgt. Bij lage pH, in een zure oplossing, is goud positief geladen en silica negatief wat leidt tot een aantrekkende kracht tussen deze oppervlakken.

Verder hebben we in dit hoofdstuk gezien dat er zelfs aantrekking kan optreden tussen twee positief geladen of twee negatief geladen oppervlakken wanneer de grootte van de oppervlaktelading op de twee oppervlakken sterk verschilt. Of er in zo'n geval afstoting of aantrekking zal optreden is alleen te voorspellen wanneer precies bekend is op welke manier de oppervlaktelading tot stand komt en of deze constant is als de oppervlakken elkaar naderen.

In hoofdstuk vier is gemeten aan met polymeren bedekte kolloïden. Polymeren zijn lange spaghetti-achtige moleculen die vaak worden gebruikt om kolloïden te stabiliseren. We hebben in de inleiding gezien dat lading op kolloïden de deeltjes kan stabiliseren doordat de deeltjes elkaar afstoten. Wanneer polymeren op kolloïden worden geadsorbeerd, kunnen de kolloïden elkaar ook niet meer heel dicht naderen. Door zo'n polymeerbarrière worden de kolloïden dus ook gestabiliseerd. In dit hoofdstuk zijn de krachten bestudeerd tussen kolloïden bedekt met polymeren van verschillende ketenlengte en bij verschillende pH waarden.

Verder is gekeken naar de krachten die optreden wanneer twee oppervlakken zo sterk op elkaar gedrukt worden dat de polymeerketens met elkaar verstrikt raken, en ook de krachten die nodig zijn om de oppervlakken dan weer uit elkaar te halen zijn gemeten. Deze hechting (adhesie) is sterker naarmate de polymeren langer zijn en er meer polymeer op het oppervlak zit. Beneden een bepaalde ketenlengte treedt er geen adhesie op. Naast de specifieke polymeereffecten blijkt ook de lading van het deeltje nog een grote rol te spelen.

In hoofdstuk vijf kijken we naar de wisselwerking tussen oppervlakken die bedekt zijn met zure of basische groepen. Dit is gedaan om een beter inzicht te krijgen in de rol die dit soort groepen spelen in de hechting. Hechting van deeltjes aan oppervlakken is van direct belang voor industriële toepassingen. Bijvoorbeeld bij het maken van TLbuizen of beeldschermen wil men een dunne laag fosforescerende deeltjes op een vast oppervlak aan brengen. Dit kan men doen door de TL-buis onder te dompelen in een suspensie van deze deeltjes. De suspensie moet stabiel blijven dat wil zeggen de deeltjes moeten elkaar niet aantrekken. Voor de hechting van de deeltjes aan de TL-buis of het televisiescherm is er juist wel attractie nodig tussen de deeltjes en het glasoppervlak. Wanneer men weet welke rol oppervlaktegroepen spelen in de hechting kunnen deze processen beter gestuurd worden. Het zal dan ook niet verbazen dat dit onderzoek mede dankzij de steun van Philips tot stand kwam.

Het aantal zure of basische groepen per oppervlakte-eenheid en de stabiliteit van de lagen die gemaakt zijn bleek sterk af te hangen van de voorbehandeling van de oppervlakken.

De hechting of adhesie tussen de verschillende lagen is steeds pH-afhankelijk en is het sterkst tussen zure en basische groepen. De gemeten adhesie was laag vergeleken met literatuurwaarden. Dit wordt waarschijnlijk veroorzaakt door de ruwheid van de oppervlakken waardoor het daadwerkelijke contactoppervlak tussen deeltjes en oppervlak veel kleiner is dan in het geval van gladde oppervlakken.

Uit het werk beschreven in dit proefschrift is ondermeer gebleken dat de bestaande theorie die gebruikt wordt om het gedrag van kolloïden te beschrijven niet in alle gevallen afdoende is. We hebben bijvoorbeeld de Van der Waals interactie niet kunnen aantreffen in de metingen. Verder bleek dat de "eenvoudige" elektrostatische interactie tussen oppervlakken erg gecompliceerd kan worden wanneer de oppervlakken niet precies gelijk zijn. De kloof tussen de bestaande theorie en de praktijkwaarnemingen wordt vooral veroorzaakt doordat de theorie vrijwel altijd uitgaat van perfect gladde en egale oppervlakken terwijl in de praktijk kolloïden vaak een ruw oppervlak hebben. Door deze oppervlakteruwheid wordt het echte contactoppervlak verkleind en kunnen korte afstandsinteracties verborgen blijven. De ruwheid kan op deze manier een grote invloed hebben op de wisselwerkingen en adhesie tussen oppervlakken, maar er is nog maar weinig theorie die dit soort effecten behandelt.

Tot slot kan worden opgemerkt dat door de ontwikkeling van de AFM tot een krachtmeetapparaat er nieuwe experimenten kunnen worden gedaan aan systemen die tot voor kort niet toegankelijk waren. Dit kan eraan bijdragen om de kloof tussen theorie en praktijk te verkleinen.

Levensloop

Marcel Giesbers werd geboren op 20 september 1963 te Arnhem. Na het doorlopen van de middelbare school (Kardinaal de Jong MAVO te Arnhem, HAVO en VWO aan het Thomas à Kempis College te Arnhem) vervulde hij de militaire dienstplicht bij het Korps Gele Rijders. Aan de Internationale Agrarische Hogeschool Larenstein afdeling laboratoriumtechniek koos Marcel voor de chemische oriëntatie. Hij sloot deze studie af met een stage en afstudeeropdracht bij het Laboratorium voor Fysische Chemie en Kolloïdkunde in Wageningen. Het onderwerp van zijn stage bij Ab van der Linde was "stromingspotentiaalmetingen in alcohol - water mengsels". De afstudeeropdracht bij Janet van Vreeswijk (aio Willem Norde) had als onderwerp "Vetzuurbinding aan elastine". Vanaf 1991 werkte Marcel bij dit laboratorium aan verschillende onderzoeksprojecten. In 1995 startte hij er met het promotie-onderzoek "Kolloidale krachten bestudeerd met Atomic Force Microscopy" waarvan u nu het resultaat in handen hebt. Sinds 1 Mei 2000 is Marcel werkzaam aan de Universiteit Utrecht bij de vakgroep Moleculaire Biofysica van het Debye instituut.

TOT SLOT,

Met het verschijnen van dit proefschrift komt voor mij een einde aan een lange periode bij "fysische en kolloïdchemie". Het is een tijd waarop ik met veel plezier terugkijk. De grote club mensen en hun diversiteit maakt fysko tot een prima werkplek en daarom wil ik allereerst IEDEREEN op de vakgroep bedanken.

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