Chemical and physical surface properties studied with scanning force microscopy
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Chapter Seven

Summary

Understanding phenomena and processes like friction, adhesion, heterogeneous catalysis, (bio)compatibility, chemical recognition and the chemical modification of surfaces requires knowledge of the chemical nature of the surfaces and the interaction between chemical functionalities at the molecular scale. The aim of this thesis is the chemical and physical characterization of surfaces and surface interactions, using Scanning Force Microscopy (SFM) in order to improve the insight into the above-mentioned processes and phenomena. Although the invention of the SFM has led to a whole class of new instruments probing a variety of surface properties such as friction, adhesion, magnetism charge, hardness etc. and has thereby provided new insights in physics, biology, chemistry and materials science, the surface chemistry has remained inaccessible.

In chapter 1 the approach to introducing chemical specificity into conventional SFM is discussed. The concept is based on providing a chemically specific interaction between the SFM probe and the surface that bears the chemical functionality of interest. This can be achieved by chemical modification of the SFM probe with functional groups that enter into the specific interaction.

In chapter 2 the basic principles of Scanning Force Microscopy with Chemical Specificity (SFMC) are demonstrated on the basis of a well-defined model system. Self-assembly of ω-functionalized n-alkanethiol compounds is used to chemically modify the SFM probes and substrates with a variety of functional groups (CH₃, OH, NH₂, COOH, CONH₂). The intermolecular interactions, i.e., hydrogen bonding and van der Waals forces between the groups on the probe and substrate are quantified by measuring the adhesion forces via force–distance curves. The magnitude of the adhesion forces is found to depend on the exact chemical nature of the surface functional groups. The adhesive interactions can be described theoretically with the Johnson–Kendall–Roberts theory of adhesion mechanics. Using this theory, important (thermodynamic) quantities, such as surface and interfacial free energies, the number of interacting molecules and single-bond forces, can be deduced from the experimental data. A good agreement is found between this JKR-theory and a recently developed statistical analysis of the adhesion force distribution, which also allows the calculation of single-bond forces and the number of interacting molecules. For the variety of tip–substrate combinations, the friction coefficients were determined from the relationship between the friction forces and the applied load, and a direct correlation between the friction and adhesion forces is demonstrated. The sensitivity of the adhesion and friction forces to the chemical nature of the sample surface is used to chemically image the distribution of functional groups. Patterns containing up to three different functional groups were successfully imaged with predictable contrast with a lateral resolution of 100 nm. The contributions of the surface
mechanical properties and the medium to the adhesion and friction force contrast between functional groups are discussed.

In chapter 3, electrostatic interactions between the chemically modified probes and substrates are exploited to identify and characterize ionizable functional groups on the basis of their acid–base behaviour. The adhesion forces are measured as a function of the pH, resulting in a so-called adhesion force titration curve. The adhesion forces are found to depend on the state of ionization of the functional groups. The local degree of ionization and the surface pK-values are determined from this adhesion force titration curve. The electric double layer, arising due to the presence of an electrolyte, is probed and the calculated Debye lengths are found to agree with theoretical calculations. The dependence of the friction forces on the ionization is used to directly image the ionization state of the surface functionalities. Moreover, the difference in ionization behaviour of acids and bases is used to differentiate and specifically image acidic and basic moieties bound to the same substrate surface.

Chapter 4 demonstrates the ability of SFMC to chemically image surfaces with a lateral resolution better than 100 nm, using microphase-separated block copolymers as model substrates. The lamellar structure of a polystyrene–poly(2-vinylpyridine) phase-separated block copolymer is successfully imaged in the friction force mode with a contrast corresponding to the chemical nature of the two constituting blocks. A chemical resolution of 25 nm in the lateral dimension is experimentally obtained.

In chapter 5 the application of SFMC to study surface chemical reactions is reported. The local reaction conversion of a model system, viz., the reaction of butyl isocyanate with surface-bound hydroxyl and carboxylic acid groups, is monitored by measuring the adhesion forces as a function of time. The distribution of reacted (and unreacted) groups is directly monitored by chemically specific friction force imaging. As an example, SFMC is applied to study the surface modification reaction of low-density polyethylene upon etching with chromic acid.

A second application of SFMC is demonstrated in chapter 6, which presents the chemical characterization of adsorbed protein layers (α-lactalbumin and lysozyme). Non-specific protein–protein interactions between protein-coated SFM probes and substrates are measured as a function of the pH. The adhesion forces show a dependency on the ionization state of the amino acid side chains and the overall adhesion force titration curve is found to compare favourably with the protein titration curve, calculated on the basis of the amino acid content and the intrinsic pK_s-values. The isoelectric point (IEP) is determined from the adhesion force titration curve and is found to be equal to the IEP of the proteins in solution as determined by iso-electric focussing. The adhesion forces depend linearly on the protein's net charge, suggesting that electrostatic interactions dominate the total protein–protein interaction. By using different-force specific probes (CH3, SO3H, OH) the qualitative contributions of hydrophobic, ion and acidic groups, respectively, are characterized.

In chapter 6 boundary lubrication of polymeric sulphides, is described. The effect of friction and adhesion is to increase, while the velocity at which the transition occurs is determined. The friction forces are used to directly image the ionization state of the surface functionalities. Moreover, the difference in ionization behaviour of acids and bases is used to differentiate and specifically image acidic and basic moieties bound to the same substrate surface.

The approach of modifying the probe tips to control the chemical interactions with the surface groups of various materials has resulted in the development of new techniques for the study of intermolecular interactions, such as supramolecular chemistries and biological systems.
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hydrophobic, ion–ion and dipolar (including hydrogen bonding) interactions, respectively, are evaluated, revealing that the ion–dipole interaction dominates the adhesive protein–protein interaction.

In chapter 7, the application of SFMC in a nanotribological study of a boundary lubricant, consisting of self-assembled monolayers of unsymmetrical dialky sulphides, is described. The adhesion forces between dialky sulphide-coated SFM probes and substrates show a direct correlation with variations in chain length, as a result of chain interdigitation. The friction force as a function of the sliding velocity shows a remarkable behaviour; upon increase of the velocity the friction forces initially increase, followed by decrease after reaching a maximum. The absolute friction forces are found to increase with increasing external load. Furthermore, the velocity at which the maximum friction occurs shifts to lower values with increasing external load but shifts to higher values as the chain length of the molecules increases (at constant external load). To explain these phenomena, a theoretical model which includes chain interdigitation is developed. Only the experimentally observed increase in critical velocity with increasing chain length cannot be accounted for by the model and is attributed to shear-induced phase transitions in the monolayer. The dependence of the adhesion and friction forces on the chain length was used to differentiate between chemically similar dialky sulphides of different length in the imaging of patterned surfaces containing up to three different dialky sulphides. The influence of the surrounding medium on the adhesion and friction was addressed by performing measurements in different solvents (ethanol, n-octane, water).

The approach to introduce chemical specificity into conventional SFM by modifying the probes with functional groups that enter into a specific interaction with surface groups of interest has proven to be a versatile and simple method. The applications of SFMC described in this thesis demonstrate its potential to become an important research tool for enhancing the insights in existing and new problems in various fields within chemistry, physics and biology. This technique will make a significant contribution to opening up new, future research areas like in supramolecular chemistry and nanotechnology.