Effects of the N, O, and S heteroatoms on the adsorption and desorption of asphaltenes on silica surface: A molecular dynamics simulation

The adsorption and desorption of asphaltene on silica surface is highly dependent on the heteroatoms present in its structure. Herein, some model asphaltene molecules with different heteroatoms (i.e., N, O, S) at different positions (in the aromatic cores, in the middle and termination of alkane side chains) are selected as the adsorbates to investigate their adsorption and desorption behaviors on silica surface through molecular dynamics (MD) simulation. Results reveal that the characteristic adsorption configuration of asphaltenes is ascribed to the competition between the asphaltene-silica interaction and π–π stacking interaction among the asphaltene polyaromatic rings. The presence of heteroatoms is found to be able to strengthen the interactions between asphaltenes and silica, depending on their type and location. For example, the terminal polar groups, especially the carboxyl (COOH), exhibit the greatest contribution to the electrostatic interaction (increasing from −81 to −727 kJ/mol). The S atoms are also found to increase the van der Waals interaction energies by 25%. According to the equilibrium desorption conformation and density profile, the presence of heteroatoms is found to significantly hinder the desorption of asphaltenes from silica due to the enhanced polar interactions. The impeded desorption is also confirmed by the slower detachment of asphaltenes based on the time-dependent interaction energies and center of mass (COM) distances analysis. Additionally, the terminal polar groups lead to extraordinary desorption properties of asphaltenes. It is observed that the strong asphaltene-silica and asphaltene-water interactions coexist in these systems due to the high polarity and hydrophilicity of the terminal polar groups.

Structural Investigation of a Self-Cross-Linked Chitosan/Alginate Dialdehyde Multilayered Film with In Situ QCM-D and Spectroscopic Ellipsometry

A chitosan/alginate dialdehyde multilayered film was fabricated using the layer-by-layer assembly method. Besides electrostatic interaction that promotes alternate adsorption of the oppositely charged polyelectrolytes, the Schiff base reaction between the amine groups on chitosan and the aldehyde groups on alginate dialdehyde provides a covalently cross-linked film, which after reduction by sodium cyanoborohydride is stable under both acidic and alkaline conditions. Moreover, the cross-linked film is responsive to changes in pH and addition of multivalent salts. The structural properties of the multilayered film such as thickness, refractive index, and water content were examined using simultaneous quartz crystal microbalance with dissipation monitoring and spectroscopic ellipsometry.
An engineered cell-imprinted substrate directs osteogenic differentiation in stem cells

A cell-imprinted poly(dimethylsiloxane)/hydroxyapatite nanocomposite substrate was fabricated to engage topographical, mechanical, and chemical signals to stimulate and boost stem cell osteogenic differentiation. The physicochemical properties of the fabricated substrates, with nanoscale resolution of osteoblast morphology, were probed using a wide range of techniques including scanning electron microscopy, atomic force microscopy, dynamic mechanical thermal analysis, and water contact angle measurements. The osteogenic differentiation capacity of the cultured stem cells on these substrates was probed by alizarin red staining, ALP activity, osteocalcin measurements, and gene expression analysis. The outcomes revealed that the concurrent roles of the surface patterns and viscoelastic properties of the substrate provide the capability of directing stem cell differentiation toward osteogenic phenotypes. Besides the physical and mechanical effects, we found that the chemical signaling of osteoinductive hydroxyapatite nanoparticles, embedded in the nanocomposite substrates, could further improve and optimize stem cell osteogenic differentiation.

Fuel-independent and membrane-less self-charging biosupercapacitor

We present a fuel-independent self-charging biosupercapacitor comprising an oxygen reducing enzymatic biocathode and an opposing bioelectrode, where the supercapacitive properties of immobilized protein were utilized. Our findings disclose a novel hybrid type of bioelectrochemical systems, which can potentially be employed as autonomous power suppliers in substrate-deficient conditions.
Interactions between apolar, basic and acidic model oils and a calcite surface

In this study, the atomic force microscopy colloidal probe technique was employed to investigate the interaction between apolar, basic and acidic model oil probes and a calcite surface in solutions containing different concentrations of NaCl, CaCl$_2$ and Na$_2$SO$_4$. In the presence of SO$_4^{2-}$, hydration and structural forces were observed between apolar model oil probes and a calcite surface on approach. Relatively low adhesion forces were observed between the basic model oil probes and the calcite surface, while higher adhesion forces were observed between the acidic model oil probes and the calcite surface. Furthermore, the adhesion forces between the basic model oil probes and the calcite surface significantly increased in the presence of SO$_4^{2-}$, while the adhesion force between the acidic model oil probes and the calcite surface decreased in the presence of Ca$^{2+}$ or SO$_4^{2-}$. The differences in the adhesion forces are related to electrostatic attraction and ion bridging forces between the model oil probes and the calcite surface.

Salt-Induced Control of the Grafting Density in Poly(ethylene glycol) Brush Layers by a Grafting-to Approach

In this work, a method to obtain control of the grafting density during the formation of polymer brush layers by the grafting-to method of thiolated poly(ethylene glycol) onto gold is presented. The grafting density of the polymer chains was adjusted by adding Na$_2$SO$_4$ in concentrations between 0.2 and 0.9 M to the aqueous polymer solution during the grafting process. The obtained grafting densities ranged from 0.26 to 1.60 chains nm$^{-2}$, as determined by surface plasmon resonance. The kinetics of the grafting process were studied in situ by a quartz crystal microbalance with dissipation, and
a mushroom to brush conformational transition was observed when the polymer was grafted in the presence of Na2SO4. The transition from mushroom to brush was only observed for long periods of grafting, highlighting the importance of time to obtain high grafting densities. Finally, the prepared brush layer with the highest grafting density showed high resistance to the adsorption of bovine serum albumin, while layers with a lower grafting density showed only limited resistance.

Surface forces between highly charged cationic polyelectrolytes adsorbed to silica: How control of pH and the adsorbed amount determines the net surface charge

Atomic force microscopy (AFM) and quartz crystal microbalance with dissipation (QCM-D) were employed to investigate the pH dependent adsorption of poly(diallyl dimethyl ammonium chloride) (polyDADMAC) to silica surfaces as well as the surface forces between these layers. It was found that polyDADMAC adopted a relatively flat conformation when adsorbed to a silica surface, and that the adsorbed amount increased with increasing pH. From the surface force measurements it is evident that the surface undergoes a charge reversal upon saturation with polyDADMAC, at the three different investigated pH values and that some degree of charge regulation of the silica surface takes place during the adsorption process. Finally, the overcharging phenomenon is discussed in terms of a geometrical mismatch due to the different average spacing between the surface charges on the silica surface and the size of the polyDADMAC monomer.
Electrical Double-Layer and Ion Bridging Forces between Symmetric and Asymmetric Charged Surfaces in the Presence of Mono- and Divalent Ions

An atomic force microscope, employing the colloidal probe technique, was used to study the interactions between six different combinations of silane-functionalized silica surfaces in NaCl and CaCl₂ solutions. The surfaces consisted of monolayers of the apolar trimethoxy(octyl)silane, the positively charged (3-aminopropyl)trimethoxysilane, and the negatively charged (3-mercaptopropyl)trimethoxysilane. The interactions between the three symmetric systems, as well as between the three asymmetric combinations of surfaces, were measured and compared to calculated electrical double-layer forces. The results demonstrated that the long-range interactions between the surfaces in all cases were dominated by double-layer forces, while short-range interactions, including adhesion, were dominated by ion bridging forces in the cases where both interaction surfaces favored adsorption of calcium ions. The study thus also demonstrates how surface force studies in mono- and divalent salt solutions can be used as an analytical tool for probing specific functional groups on heterogeneous surfaces.

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Organisations: Department of Chemistry, Centre for oil and gas – DTU, Center for Energy Resources Engineering, Department of Chemical and Biochemical Engineering, CERE – Center for Energy Resources Engineering
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Hofmeister Effect on PNIPAM in Bulk and at an Interface: Surface Partitioning of Weakly Hydrated Anions

The effect of sodium fluoride, sodium trichloroacetate, and sodium thiocyanate on the stability and conformation of poly(N-isopropylacrylamide), in bulk solution and at the gold-aqueous interface, is investigated by differential scanning calorimetry, dynamic light scattering, quartz crystal microbalance, and atomic force microscopy. The results indicate a surface partitioning of the weakly hydrated anions, i.e., thiocyanate and trichloroacetate, and the findings are discussed in terms of anion-induced electrostatic stabilization. Although attractive polymer-ion interactions are suggested for thiocyanate and trichloroacetate, a salting-out effect is found for sodium trichloroacetate. This apparent contradiction is explained by a combination of previously suggested mechanisms for the salting-out effect by weakly hydrated anions.

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Surface forces between rough and topographically structured interfaces

Within colloidal science, direct or indirect measurements of surface forces represent an important tool for developing a fundamental understanding of colloidal systems, as well as for predictions of the stability of colloidal suspensions. While the general understanding of colloidal interactions has developed significantly since the formulation of the DLVO theory, many problems still remain to be solved. One concrete problem is that the current theory has been developed for interaction between flat and chemically homogenous surfaces, which is in contrast to the surfaces of most natural and manufactured materials, which possess topographical variations. Further, with technological advances in nanotechnology, fabrication of nano- or micro-structured surfaces has become increasingly important for many applications, which calls for a better understanding of the effect of surface topography on the interaction between interfaces. This paper presents a review of the current state of understanding of the effect of surface roughness on DLVO forces, as well as on the interactions between topographically structured hydrophobic surfaces in water. While the first case is a natural choice because it represents the most general description of colloidal interactions, the second case represents examples of how intentionally built-in surface structures can significantly alter the interactions between surfaces.

General information

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Contributors: Thormann, E.
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Research output: Contribution to journal › Journal article – Annual report year: 2016 › Research › peer-review

Thermo-responsive diblock and triblock cationic copolymers at the silica/aqueous interface: A QCM-D and AFM study

The properties of synthesized diblock poly(N-isopropylacrylamide)-poly(3-acrylamidopropyltrimethylammonium chloride) and triblock methoxy-poly(ethylene glycol)-poly(N-isopropylacrylamide)-poly(3-acrylamidopropyl)trimethylammonium chloride) cationic copolymers at the silica/aqueous interface are investigated using quartz crystal microbalance with dissipation monitoring (QCM-D) and atomic force microscopy (AFM). Moreover, dynamic light scattering is employed to
assess the copolymers in terms of the hydrodynamic size and interchain aggregation. Although viscoelastic Voigt modeling of the QCM-D data suggests a comparable layer thickness for the copolymers on the silica surface, the AFM imaging and colloidal probe measurements reveal significant differences in surface coverage and thickness of the layers, which are discussed and compared with respect to the stabilization effect by the hydrophilic poly(ethylene glycol) block.

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Organisations: Department of Chemistry, University of Oslo
Contributors: Moghaddam, S. Z., Zhu, K., Nyström, B., Thormann, E.
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Web of Science (2017): Impact factor 5.091
Web of Science (2017): Indexed yes
Original language: English
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**Binding of human serum albumin to liposomes studied by fluorescence correlation spectroscopy**

**General information**
Publication status: Published
Organisations: Department of Micro- and Nanotechnology, Colloids and Biological Interfaces, Department of Chemistry
Contributors: Kristensen, K., Urquhart, A., Thormann, E., Andresen, T. L.
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Research output: Contribution to conference › Poster – Annual report year: 2016 › Research › peer-review

**Binding of human serum albumin to PEGylated liposomes: insights into binding numbers and dynamics by fluorescence correlation spectroscopy**

Liposomes for medical applications are often administered by intravenous injection. Once in the bloodstream, the liposomes are covered with a "protein corona", which impacts the behavior and eventual fate of the liposomes. Currently, many aspects of the liposomal protein corona are not well understood. For example, there is generally a lack of knowledge about the liposome binding affinities and dynamics of common types of blood plasma proteins. Fluorescence correlation spectroscopy (FCS) is a powerful experimental technique that potentially can provide such knowledge. In this study, we have used FCS to investigate the binding of human serum albumin (HSA) to standard types of PEGylated fluid-phase liposomes (consisting of DOPC and DOPE-PEG2k) and PEGylated gel-phase liposomes (consisting of DSPC and DSPE-PEG2k) with various PEG chain surface densities. We detected no significant binding of HSA to the PEGylated fluid-phase liposomes. In contrast, we found that HSA bound tightly to the PEGylated gel-phase liposomes, although only a low number of HSA molecules could be accommodated per liposome. Overall, we believe that our data provides a useful benchmark for other researchers interested in studying the liposomal protein corona.

**General information**
Publication status: Published
Effect of Aluminum Substrate Surface Modification on Wettability and Freezing Delay of Water Droplet at Subzero Temperatures

In this study, we have investigated the freezing delay of a water droplet on precooled substrates of an aluminum alloy that is commonly used for heat-exchanger fins. The surfaces of the substrates were modified to obtain surfaces with different hydrophilicity/hydrophobicity and different surface chemistry but without significantly modifying the surface topography. The freezing delays and water contact angles were measured as a function of the substrate temperature and the results were compared to the predictions of the heterogeneous ice nucleation theory. Although the trends for each sample followed the trend in this theory, the differences in the extents of freezing delays were in apparent disagreement with the predictions. Concretely, a slightly hydrophilic substrate modified by (3-aminopropyl) triethoxysilane (APTES) showed longer freezing delays than both more hydrophilic and more hydrophobic substrates. We suggest that this is because this particular surface chemistry prevents ice formation at the interface of the substrate, prior to the deposition of the water droplet. On the basis of our results, we suggest that not only wettability and topography but also the concrete surface chemistry plays a significant role in the kinetics of the ice formation process when a water droplet is placed on a precooled substrate.

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Organisations: Department of Chemistry, Aalborg University
Contributors: Rahimi, M., Afshari, A., Thormann, E.
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Hofmeister effect on thermo-responsive poly(propylene oxide) in H₂O and D₂O

The Hofmeister effect of NaSCN, NaCl and NaF on poly(propylene oxide) solutions in H₂O and D₂O is studied. The effect of the solvent substitution is shown to vary for different salts and we suggest that this is due to a change in the polymer accessible surface area and ion hydration.

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Organisations: Department of Chemistry
Contributors: Moghaddam, S. Z., Thormann, E.
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Web of Science (2016): Indexed yes
Original language: English
DOIs: 10.1039/c6ra02703b
Source: FindIt
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Hofmeister effect on thermo-responsive poly(propylene oxide): Role of polymer molecular weight and concentration

Although a vast amount of research has been dedicated to investigate the Hofmeister effect on the stability of polymer solutions, a clear understanding of the role of polymer properties in this phenomenon is still missing. Here, the Hofmeister effect of NaCl (destabilizing) and NaSCN (stabilizing) salts on aqueous solutions of poly(propylene oxide) (PPO) is studied. Four different molecular weights of PPO were investigated, to determine how the variation in the polymer coil size affects the Hofmeister effect. The investigation was further conducted for different PPO concentrations, in order to understand the effect of inter-chain interactions on the response to addition of salt. The temperature-driven phase separation of the solutions was monitored by differential scanning calorimetry, which provides the precise value of the phase separation temperature, as well as the enthalpy change accompanied with the transition. It was observed that increasing the molecular weight weakens the effect of the both salts, which is interpreted in terms of a scaling law between the molecular weight and the accessible surface area of the polymers. Increasing the PPO concentration further diminished the NaCl effect, but amplified the NaSCN effect. This difference is attributed to an electrostatic stabilization mechanism in the case of NaSCN.

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Contributors: Moghaddam, S. Z., Thormann, E.
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Release of Crude Oil from Silica and Calcium Carbonate Surfaces: On the Alternation of Surface and Molecular Forces by High- and Low-Salinity Aqueous Salt Solutions

Adsorption and desorption of a North Sea crude oil to silica and calcium carbonate surfaces were studied by a quartz crystal microbalance, while the bare surfaces and adsorbed oil layers were characterized by atomic force microscopy and contact angle measurements. Water contact angles were measured on the bare surfaces, surfaces with an adsorbed oil layer, and surfaces after being exposed to aqueous salt solutions. This showed that the silica surface became more hydrophobic after oil adsorption, while the wettability of the calcium carbonate surface was not significantly changed by adsorption of an oil layer. A surface energy component analysis based on the acid base theory showed that oil adsorption on the surfaces depends upon apolar, acidic, and basic oil components of the crude oil and that the adsorbed oil components differ for adsorption to silica and calcium carbonate. Desorption of the crude oil was investigated by exposing the surfaces with an adsorbed oil layer to a series of NaCl and CaCl2 solutions of decreasing salt concentrations. Here, it was found that the oil release from silica was achieved only by injections of low-salinity solutions, and it is suggested that this observation is due to an expansion of the electrical double layer. The oil release from calcium carbonate was achieved by injection of both high- and low-salinity solutions of NaCl but not injection of a high-salinity solution of CaCl2. These observations are attributed to dissolution of calcium carbonate or reduction in ion bridging in the presence of high-salinity NaCl, while the low-salinity effect again was attributed to an expansion of the electrical double layer.

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Web of Science (2016): Impact factor 3.091
Web of Science (2016): Indexed yes
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Charge regulation and energy dissipation while compressing and sliding a cross-linked chitosan hydrogel layer

Interactions between a silica surface and a surface coated with a grafted cross-linked hydrogel made from chitosan/PAA multilayers are investigated, utilizing colloidal probe atomic force microscopy. Attractive double-layer forces are found to dominate the long-range interaction over a broad range of pH and ionic strength conditions. The deduced potential at the hydrogel/aqueous interface is found to be very low. This situation is maintained in the whole pH-range investigated, even though the degree of protonation of chitosan changes significantly. This demonstrates that pH-variations change the concentration of counterions within the hydrogel to keep the interior close to uncharged, which is similar to what has been observed for polyelectrolyte brushes. Changes in pH and ionic strength affect the adhesion force and the friction force between the silica surface and the hydrogel layer, but not the friction coefficient. This suggests that the main energy dissipation mechanism arises from processes occurring within the hydrogel layer, rather than at the silica/hydrogel interface.
interface, and we suggest that it is related to stretching of polymer chains between the cross-linking points. We also find that an increased cross-linking density, from 40% to 100%, in the hydrogel reduces the friction coefficient.

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Organisations: Department of Chemistry, KTH - Royal Institute of Technology, SP Technical Research Institute of Sweden
Contributors: Liu, C., Thormann, E., Tyrode, E., Claesson, P. M.
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Web of Science (2015): Indexed yes
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**Hofmeister effect of salt mixtures on thermo-responsive poly(propylene oxide)**
The Hofmeister series is a classification of ions regarding their ability to stabilize or destabilize aqueous solutions of proteins, polymers and other molecules which are partly miscible with water. In this study, we employ differential scanning calorimetry to investigate how the stability of aqueous solutions of poly(propylene oxide) is affected by mixtures of ions with different location in the Hofmeister series. Our results show that the Hofmeister effects of pure salt species are not always linearly additive and that the relative effect of some ions can be reversed depending on the composition of the salt mixture as well as by the absolute and relative concentration of the different species. We suggest that these results can lead to a better understanding of the potential role of the Hofmeister effect in regulation of biological processes, which does always take place in salt mixtures rather than solutions containing just single salt species.

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Contributors: Moghaddam, S. Z., Thormann, E.
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Source-ID: 274094404
Multi-function anti-fouling bio-active surfaces

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Contributors: Ortiz, R., Thormann, E.
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Direct measurement of colloidal interactions between polyaniline surfaces in a uv-curable coating formulation: the effect of surface hydrophilicity/ hydrophobicity and resin composition
The interactions between polyaniline particles and polyaniline surfaces in polyester acrylate resin mixed with 1,6-hexanediol diacrylate monomer have been investigated using contact angle measurements and the atomic force microscopy colloidal probe technique. Polyaniline with different characteristics (hydrophilic and hydrophobic) were synthesized directly on spherical polystyrene particles of 10 μm in diameter. Surface forces were measured between core/shell structured polystyrene/polyaniline particles (and a pure polystyrene particle as reference) mounted on an atomic force microscope cantilever and a pressed pellet of either hydrophilic or hydrophobic polyaniline powders, in resins of various polymer:monomer ratios. A short-range purely repulsive interaction was observed between hydrophilic polyaniline (doped with phosphoric acid) surfaces in polyester acrylate resin. In contrast, interactions between hydrophobic polyaniline (doped with n-decyl phosphonic acid) were dominated by attractive forces, suggesting less compatibility and higher tendency for aggregation of these particles in liquid polyester acrylate compared to hydrophilic polyaniline. Both observations are in agreement with the conclusions from the interfacial energy studies performed by contact angle measurements.

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Organisations: Department of Chemistry, KTH - Royal Institute of Technology
Contributors: Jafarzadeh, S., Claesson, P. M., Pan, J., Thormann, E.
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Web of Science (2014): Impact factor 4.457
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Original language: English
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**Self-assembly of long chain fatty acids: Effect of a methyl branch**

The morphology and molecular conformation of Langmuir-Blodgett deposited and floating monolayers of a selection of straight chain (eicosanoic acid, EA), iso (19-methyl eicosanoic acid, 19-MEA), and anteiso (18-methyl eicosanoic acid, 18-MEA) fatty acids have been investigated by Vibrational Sum Frequency Spectroscopy (VSFS), AFM imaging, and the Langmuir trough. While the straight chain fatty acid forms smooth, featureless monolayers, all the branched chain fatty acids display 10-50 nm sized domains (larger for 19-MEA than the 18-MEA) with a homogeneous size distribution. A model is suggested to explain the domain formation and size in terms of the branched fatty acid packing properties and the formation of hemispherical caps at the liquid-air interface. No difference between the chiral (S) form and the racemic mixture of the 18-MEA is observed with any of the utilized techniques. The aliphatic chains of the straight chain fatty acids appear to be oriented perpendicular to the sample surface, based on an orientational analysis of VSFS data and the odd/even effect. In addition, the selection of the subphase (neat water or CdCl2 containing water buffered to pH 6.0) used for the LB-deposition has a profound influence on the monolayer morphology, packing density, compressibility, and conformational order. Finally, the orientation of the 19-MEA dimethyl moiety is estimated, and a strategy for performing an orientational analysis to determine the complete molecular orientation of the aliphatic chains of 19-MEA and 18-MEA is outlined and discussed. This journal is © the Partner Organisations 2014.

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Research > peer-review

**Surface grafted chitosan gels. Part II. Gel formation and characterization**

Responsive biomaterial hydrogels attract significant attention due to their biocompatibility and degradability. In order to make chitosan based gels, we first graft one layer of chitosan to silica, and then build a chitosan/poly(acrylic acid) multilayer using the layer-by-layer approach. After cross-linking the chitosan present in the polyelectrolyte multilayer, poly(acrylic acid) is partly removed by exposing the multilayer structure to a concentrated carbonate buffer solution at a high pH, leaving a surface-grafted cross-linked gel. Chemical cross-linking enhances the gel stability against detachment and decomposition. The chemical reaction between gluteraldehyde, the cross-linking agent, and chitosan was followed in situ using total internal reflection Raman (TIRR) spectroscopy, which provided a molecular insight into the complex reaction mechanism, as well as the means to quantify the cross-linking density. The amount of poly(acrylic acid) trapped inside the surface grafted films was found to decrease with decreasing cross-linking density, as confirmed in situ using TIRR, and ex situ by Fourier transform infrared (FTIR) measurements on dried films. The responsiveness of the chitosan-based gels with respect to pH changes was probed by quartz crystal microbalance with dissipation (QCM-D) and TIRR. Highly cross-linked gels show a small and fully reversible behavior when the solution pH is switched between pH 2.7 and 5.7. In contrast, low cross-linked gels are more responsive to pH changes, but the response is fully reversible only after the first exposure to the acidic solution, once an internal restructuring of the gel has taken place. Two distinct pKa's for both chitosan and poly(acrylic acid), were determined for the cross-linked structure using TIRR. They are associated with populations of chargeable groups displaying either a bulk like dissociation behavior or forming ionic complexes inside the hydrogel film. © 2014 American Chemical Society.

**General information**

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Surface grafted chitosan gels. Part I. Molecular insight into the formation of chitosan and poly(acrylic acid) multilayers

Composite polyelectrolyte multilayers of chitosan and low molecular weight poly(acrylic acid) (PAA) have been assembled by sequential adsorption as a first step toward building a surface anchored chitosan gel. Silane chemistry was used to graft the first chitosan layer to prevent film detachment and decomposition. The assembly process is characterized by nonlinear growth behavior, with different adsorption kinetics for chitosan and PAA. In situ analysis of the multilayer by means of surface sensitive total internal reflection Raman (TIRR) spectroscopy, combined with target factor analysis of the spectra, provided information regarding composition, including water content, and ionization state of weak acidic and basic groups present in the thin composite film. Low molecular weight PAA, mainly in its protonated form, diffuses into and out of the composite film during adsorption and rinsing steps. The higher molecular weight chitosan shows a similar behavior, although to a much lower extent. Our data demonstrate that the charged monomeric units of chitosan are mainly compensated by carboxylate ions from PAA. Furthermore, the morphology and mechanical properties of the multilayers were investigated in situ using atomic force microscopy operating in PeakForce tapping mode. The multilayer consists of islands that grow in lateral dimension and height during the build-up process, leading to close to exponentially increasing roughness with deposition number. Both diffusion in and out of at least one of the two components (PAA) and the island-like morphology contribute to the nonlinear growth of chitosan/PAA multilayers. © 2014 American Chemical Society.
Frictional forces between hydrophilic and hydrophobic particle coated nanostructured surfaces

Friction forces have long been associated with the famous Amontons' rule that states that the friction force is linearly dependent on the applied normal load, with the proportionality constant being known as the friction coefficient. Amontons' rule is however purely phenomenological and does not in itself provide any information on why the friction coefficient is different for different material combinations. In this study, friction forces between a colloidal probe and nanostructured particle coated surfaces in an aqueous environment exhibiting different roughness length scales were measured by utilizing the atomic force microscope (AFM). The chemistry of the surfaces and the probe was varied between hydrophilic silica and hydrophobized silica. For hydrophilic silica surfaces, the friction coefficient was significantly higher for the particle coated surfaces than on the flat reference surface. All the particle coated surfaces exhibited similar friction coefficients, from which it may be concluded that the surface geometry, and not the roughness amplitude per se, influenced the measured friction. During measurements with hydrophobic surfaces, strong adhesive forces related to the formation of a bridging air cavity were evident from both normal force and friction force measurements. In contrast to the frictional forces between the hydrophilic surfaces, the friction coefficient for hydrophobic surfaces was found to depend on the surface structure and we believe that this dependence is related to the restricted movement of the three-phase line of the bridging air cavity. For measurements using a hydrophobic surface and a hydrophilic probe, the friction coefficient was significantly smaller compared to the two homogeneous systems. A layer of air or air bubbles on the hydrophobic surface working as a lubricating layer is a possible mechanism behind this observation.

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Hyaluronan and phospholipid association in biolubrication

It is becoming increasingly clear that the outstanding lubrication of synovial joints is achieved by a sophisticated hierarchical structure of cartilage combined with synergistic actions of surface-active components present in the synovial fluid. In this work we focus on the association of two components of the synovial fluid, hyaluronan and dipalmitoyl phosphatidyl choline (DPPC), in bulk solution and at interfaces. We demonstrate that hyaluronan associates with DPPC vesicles and adsorbs to supported DPPC bilayers. The association structures formed at the interface are sufficiently stable to allow sequential adsorption of DPPC and hyaluronan, whereby promoting the formation of thick composite layers of these two components. The lubricating ability of such composite layers was probed by the AFM colloidal probe technique and found to be very favorable with low friction coefficients and high load bearing capacity. With DPPC as the last adsorbed component, a friction coefficient of 0.01 was found up to pressures significantly above what is encountered in healthy synovial joints. Hyaluronan as the last added component increases the friction coefficient to 0.03 and decreases the load bearing capacity somewhat (but still above what is needed in the synovial joint). Our data demonstrate that self-assembly structures formed by hyaluronan and phospholipids at interfaces are efficient aqueous lubricants, and it seems plausible that such self-assembly structures contribute to the exceptional lubrication of synovial joints. © 2013 American Chemical Society.

General information
Hydrophobic pore array surfaces: Wetting and interaction forces in water/ethanol mixtures

Interactions between and wetting behavior of structured hydrophobic surfaces using different concentrations of water/ethanol mixtures have been investigated. Silica surfaces consisting of pore arrays with different pore spacings and pore depths were made hydrophobic by silanization. Their static and dynamic contact angles were found to be independent of the pore depth while fewer pores on the surface, i.e. a closer resemblance to a flat surface, gave a lower contact angle. As expected, a higher amount of ethanol facilitated wetting on all the surfaces tested. Confocal Raman microscopy measurements proved both water and ethanol to penetrate into the pores. AFM colloidal probe force measurements clearly showed that formation of air cavitation was hindered between the hydrophobic surfaces in presence of ethanol, and an increase in ethanol concentration was followed by a smaller jump-in distance and a weaker adhesion force. On separation, an immediate jump-out of contact occurred. The measured forces were interpreted as being due to capillary condensation of ethanol between the surfaces giving rise to very unstable cavities immediately rupturing on surface separation.
Hydrophobic Surfaces: Topography Effects on Wetting by Supercooled Water and Freezing Delay

Hydrophobicity, and in particular superhydrophobicity, has been extensively considered to promote ice-phobicity. Dynamic contact angle measurements above 0 °C have been widely used to evaluate the water repellency. However, it is the wetting properties of supercooled water at subzero temperatures and the derived work of adhesion that are important for applications dealing with icing. In this work we address this issue by determining the temperature-dependent dynamic contact angle of microliter-sized water droplets on a smooth hydrophobic and a superhydrophobic surface with similar surface chemistry. The data highlight how the work of adhesion of water in the temperature interval from about 25 °C to below −10 °C is affected by surface topography. A marked decrease in contact angle on the superhydrophobic surface is observed with decreasing temperature, and we attribute this to condensation below the dew point. In contrast, no significant wetting transition is observed on the smooth hydrophobic surface. The freezing temperature and the freezing delay time were determined for water droplets resting on a range of surfaces with similar chemistry but different topography, including smooth and rough surfaces in either the Wenzel or the Cassie–Baxter state as characterized by water contact angle measurements at room temperature. We find that the water freezing delay time is not significantly affected by the surface topography and discuss this finding within the classical theory of heterogeneous nucleation.

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Low friction and high load bearing capacity layers formed by cationic-block-non-ionic bottle-brush copolymers in aqueous media
Efficient lubricants should be able to build surface layers that result in low friction and high load bearing capacity. In this work we show how this can be achieved in aqueous media by means of adsorption of a diblock copolymer consisting of a cationic anchor block without side chains and an uncharged and hydrophilic bottle-brush block that protrudes into solution. Surface and friction forces were measured between negatively charged silica surfaces coated with adsorbed layers of the cationic diblock copolymer, utilizing the atomic force microscope colloidal probe technique. The interactions between the surfaces coated with this copolymer in water are purely repulsive, due to a combination of steric and electrostatic double-layer forces, and no hysteresis is observed between forces measured on approach and separation. Friction forces between the diblock copolymer layers are characterized by a low friction coefficient, \( \mu \approx 0.03-0.04 \). The layers remain intact under high load and shear due to the strong electrostatic anchoring, and no destruction of the layer was noted even
under the highest pressure employed (about 50 MPa). Addition of NaCl to a concentration of 155 mM weakens the anchoring of the copolymer to the substrate surface, and as a result the friction force increases. © 2013 The Royal Society of Chemistry.
Note: Determination of torsional spring constant of atomic force microscopy cantilevers: Combining normal spring constant and classical beam theory
A technique has been developed for the calculation of torsional spring constants for AFM cantilevers based on the combination of the normal spring constant and plate/beam theory. It is easy to apply and allow the determination of torsional constants for stiff cantilevers where the thermal power spectrum is difficult to obtain due to the high resonance frequency and low signal/noise ratio. The applicability is shown to be general and this simple approach can thus be used to obtain torsional constants for any beam shaped cantilever. © 2013 AIP Publishing LLC.

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Quartz Crystal Microbalance with Dissipation (QCM-D) studies of the viscoelastic response from a continuously growing grafted polyelectrolyte layer
Poly(acrylic acid) was grown from substrates by photopolymerization, and the grafting process was monitored in situ by Quartz Crystal Microbalance with Dissipation (QCM-D) measurements in a 1:1 v/v mixture of water/ethanol. The polymerization process was monitored into the thick film region, where the change in frequency and dissipation with increasing film mass changes sign as predicted by the Voigt viscoelastic model. Our experimental data are compared with predictions of this model, and satisfactory agreement is found for low overtone numbers. The Voigt model was applied to analyze the measured changes in frequency, Δf, and dissipation, ΔD, in order to extract information on layer thickness, shear elasticity, μ, and shear viscosity, η, of the growing film. The increasing rate of changes in Δf and ΔD observed after about 150 s of polymerization was found to correlate with an increasing growth rate of the film thickness. For longer polymerization times a close to linear increase in thickness with time was observed. The sensitivity, defined as the derivatives of Δf and ΔD with respect to thickness, depends on overtone number and is different for the frequency and dissipation signals - facts that should be considered when investigating small changes in thick films used in e.g. sensor applications. © 2013 Elsevier Inc.

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Sustained frictional instabilities on nanodomed surfaces: Stick-slip amplitude coefficient

Understanding the frictional properties of nanostructured surfaces is important because of their increasing application in modern miniaturized devices. In this work, lateral force microscopy was used to study the frictional properties between an AFM nanotip and surfaces bearing well-defined nanodomes comprising densely packed prolate spheroids, of diameters ranging from tens to hundreds of nanometers. Our results show that the average lateral force varied linearly with applied load, as described by Amontons' first law of friction, although no direct correlation between the sample topographic properties and their measured friction coefficients was identified. Furthermore, all the nanodomed textures exhibited pronounced oscillations in the shear traces, similar to the classic stick-slip behavior, under all the shear velocities and load regimes studied. That is, the nanotextured topography led to sustained frictional instabilities, effectively with no contact frictional sliding. The amplitude of the stick-slip oscillations, $\sigma_f$, was found to correlate with the topographic properties of the surfaces and scale linearly with the applied load. In line with the friction coefficient, we define the slope of this linear plot as the stick-slip amplitude coefficient (SSAC). We suggest that such stick-slip behaviors are characteristics of surfaces with nanotextures and that such local frictional instabilities have important implications to surface damage and wear. We thus propose that the shear characteristics of the nanodomed surfaces cannot be fully described by the framework of Amontons' laws of friction and that additional parameters (e.g., $\sigma_f$ and SSAC) are required, when their friction, lubrication, and wear properties are important considerations in related nanodevices. © 2013 American Chemical Society.
**Tribological Properties Mapping: Local Variation in Friction Coefficient and Adhesion**

Tribological properties mapping is a new technique that extracts friction coefficient and adhesion maps obtained from lateral atomic force microscope (LAFM) images. By imaging the surface systematically as a function of load, a series of images can be tiled, and pixelwise fitted to a modified Amontons' Law to obtain friction coefficient and adhesion maps. This removes the ambiguity of friction contrast in LAFM imaging which can be a function of the load used for imaging. In ambient laboratory, air and tetradecane, a sample of Vancron®40, commercial powder metallurgical tool alloy containing nitrogen, have been scanned using a standard silicon cantilever in order to obtain tribological data. The tribological properties mapping provides unique information regarding the heterogeneous alloy microstructure as well as shedding light on the tribological behavior of the alloy.

**Adsorption and protein-induced metal release from chromium metal and stainless steel**

A research effort is undertaken to understand the mechanism of metal release from, e.g., inhaled metal particles or metal implants in the presence of proteins. The effect of protein adsorption on the metal release process from oxidized chromium metal surfaces and stainless steel surfaces was therefore examined by quartz crystal microbalance with energy dissipation monitoring (QCM-D) and graphite furnace atomic absorption spectroscopy (GFAAS). Differently charged and sized proteins, relevant for the inhalation and dermal exposure route were chosen including human and bovine serum albumin (HSA, BSA), mucin (BSM), and lysozyme (LYS). The results show that all proteins have high affinities for chromium and stainless steel (AISI 316) when deposited from solutions at pH 4 and at pH 7.4 where the protein adsorbed amount was very similar. Adsorption of albumin and mucin was substantially higher at pH 4 compared to pH 7.4 with approximately monolayer coverage at pH 7.4, whereas lysozyme adsorbed in multilayers at both investigated pH. The protein–surface interaction was strong since proteins were irreversibly adsorbed with respect to rinsing. Due to the passive nature of chromium and stainless steel (AISI 316) surfaces, very low metal release concentrations from the QCM metal surfaces in the presence of proteins were obtained on the time scale of the adsorption experiment. Therefore, metal release studies from massive metal sheets in contact with protein solutions were carried out in parallel. The presence of proteins increased the extent of metals released for chromium metal and stainless steel grades of different microstructure and alloy content, all with passive chromium(III)-rich surface oxides, such as QCM (AISI 316), ferritic (AISI 430), austentic (AISI 304, 316L), and duplex (LDX 2205).
Aggregation of Modified Celluloses in Aqueous Solution: Transition from Methylcellulose to Hydroxypropylmethylcellulose Solution Properties Induced by a Low-Molecular-Weight Oxyethylene Additive

Temperature effects on the viscosity and aggregation behavior of aqueous solutions of three different cellulose ethers: methylcellulose (MC), hydroxypropylmethylcellulose (HPMC), and ethyl(hydroxyethyl)cellulose (EHEC) were investigated using viscosity and dynamic light scattering measurements as well as cryo-TEM. In all cases, increasing temperature reduces the solvent quality of water, which induces aggregation. It was found that the aggregation rate followed the order EHEC > HPMC > MC, suggesting that cellulose ethers containing some bulky and partially hydrophilic substituents assemble into large aggregates more readily than methylcellulose. This finding is discussed in terms of the organization of the structures formed by the different cellulose ethers. The temperature-dependent association behavior of cellulose ethers was also investigated in a novel way by adding diethylene glycol monobutylether (BDG) to methylcellulose aqueous solutions. When the concentration of BDG was at and above 5 wt %, methylcellulose adopted HPMC-like solution behavior. In particular, a transition temperature where the viscosity was decreasing, prior to increasing at higher temperatures, appeared, and the aggregation rate increased. This observation is rationalized by the ability of amphiphilic BDG to accumulate at nonpolar interfaces and thus also to associate with hydrophobic regions of methylcellulose. In effect, BDG is suggested to act as a physisorbed hydrophilic and bulky substituent inducing constraints on aggregation similar to those of the chemically attached hydroxypropyl groups in HPMC and oligo(ethyleneoxide) chains in EHEC.

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Attractive double-layer forces and charge regulation upon interaction between electrografted amine layers and silica

Amine functionalities have been introduced on glassy carbon surfaces through electrografting of 4-(2-aminoethyl)benzenediazonium tetrafluoroborate. The grafted layers were characterized by ellipsometry and by nanomechanical mapping in air and aqueous solutions using the atomic force microscopy PeakForce QNM mode. The layer was found to be 2.5 nm thick with low roughness, comparable to that of the glassy carbon substrate. However, small semi-spherical features were observed in the topographical image, indicating a clustering of the grafted amine compound. The nanomechanical mapping also demonstrated some swelling of the layer in water and pointed toward an important contribution of electrostatic interactions for the tip-surface adhesion. The forces between an aminated glassy carbon surface and a μm-sized silica particle in aqueous solutions were measured at different ionic strength and pH-values. The results demonstrate that an attractive double-layer force predominates at large separations, and that the surface charge densities increase as the separation between the surfaces decreases. The degree of charge regulation on the aminated glassy carbon is significant. The relatively low surface charge density of the aminated glassy carbon is attributed to significant incorporation of counterions in the water-rich grafted layer.

Effect of Surface Depressions on Wetting and Interactions between Hydrophobic Pore Array Surfaces

The surface structure is known to significantly affect the long-range capillary forces between hydrophobic surfaces in aqueous solutions. It is, however, not clear how small depressions in the surface will affect the interaction. To clarify this, we have used the AFM colloidal probe technique to measure interactions between hydrophobic microstructured pore array surfaces and a hydrophobic colloidal probe. The pore array surfaces were designed to display two different pore spacings, 1.4 and 4.0 μm, each with four different pore depths ranging from 0.2 to 12.0 μm. Water contact angles measured on the pore array surfaces are lower than expected from the Cassie–Baxter and Wenzel models and not affected by the pore depth. This suggests that the position of the three-phase contact line, and not the interactions underneath the droplet, determines the contact angle. Confocal Raman microscopy was used to investigate whether water penetrates into the pores. This is of importance for capillary forces where both the movement of the three-phase contact line and the situation at the solid/liquid interface influence the stability of bridging cavities. By analyzing the shape of the force curves, we distinguish whether the cavity between the probe and the surfaces was formed on a flat part of the surface or in close proximity to a pore. The pore depth and pore spacing were both found to statistically influence the distance at which cavities form as surfaces approach each other and the distance at which cavities rupture during retraction.
Electrostatically Anchored Branched Brush Layers

A novel type of block copolymer has been synthesized. It consists of a linear cationic block and an uncharged bottle-brush block. The nonionic bottle-brush block contains 45 units long poly(ethylene oxide) side chains. This polymer was synthesized with the intention of creating branched brush layers firmly physisorbed to negatively charged surfaces via the cationic block, mimicking the architecture (but not the chemistry) of bottle-brush molecules suggested to be present on the cartilage surface, and contributing to the efficient lubrication of synovial joints. The adsorption properties of the diblock copolymer as well as of the two blocks separately were studied on silica surfaces using quartz crystal microbalance with dissipation monitoring (QCM-D) and optical reflectometry. The adsorption kinetics data highlight that the diblock copolymers initially adsorb preferentially parallel to the surface with both the cationic block and the uncharged bottle-brush block in contact with the surface. However, as the adsorption proceeds, a structural change occurs within the layer, and the PEO bottle-brush block extends toward solution, forming a surface-anchored branched brush layer. As the adsorption plateau is reached, the diblock copolymer layer is 46–48 nm thick, and the water content in the layer is above 90 wt %. The combination of strong electrostatic anchoring and highly hydrated branched brush structures provide strong steric repulsion, low friction forces, and high load bearing capacity. The strong electrostatic anchoring also provides high stability of preadsorbed layers under different ionic strength conditions.
Embedded proteins and sacrificial bonds provide the strong adhesive properties of gastroliths

The adhesive properties of gastroliths from a freshwater crayfish (Cherax quadricarinatus) were quantified by colloidal probe atomic force microscopy (AFM) between heavily demineralized gastrolith microparticles and gastrolith substrates of different composition. Combined AFM and transmission electron microscopy studies demonstrated that the sequential detachment and large adhesion energies that characterise the adhesive behaviour of a native gastrolith substrate are dominated by sacrificial bonds between chitin fibres and between chitin fibres and CaCO3. The sacrificial bonds were shown to be strongly related to the gastrolith proteins and when the majority of these proteins were removed by ethylenediaminetetraacetic acid (EDTA), the sequential detachment disappeared and the adhesive energy was reduced by more than two orders of magnitude. © 2012 The Royal Society of Chemistry.

Hyaluronan and phospholipids in boundary lubrication

Hyaluronan has been found to play an important role in boundary lubrication in joints, but model experiments have shown that free hyaluronan is reluctant to stay between surfaces. We show that hyaluronan, when assisted by a phospholipid bilayer, can act as a boundary lubricant, even at pressures well above those leading to breakdown of cartilage. © The Royal Society of Chemistry 2012.
Influence of Surface Topography on the Interactions between Nanostructured Hydrophobic Surfaces

Nanostructured particle coated surfaces, with hydrophobized particles arranged in close to hexagonal order and of specific diameters ranging from 30 nm up to 800 nm, were prepared by Langmuir–Blodgett deposition followed by silanization. These surfaces have been used to study interactions between hydrophobic surfaces and a hydrophobic probe using the AFM colloidal probe technique. The different particle coated surfaces exhibit similar water contact angles, independent of particle size, which facilitates studies of how the roughness length scale affects capillary forces (previously often referred to as "hydrophobic interactions") in aqueous solutions. For surfaces with smaller particles (diameter <200 nm), an increase in roughness length scale is accompanied by a decrease in adhesion force and bubble rupture distance. It is suggested that this is caused by energy barriers that prevent the motion of the three-phase (vapor/liquid/solid) line over the surface features, which counteracts capillary growth. Some of the measured force curves display extremely long-range interaction behavior with rupture distances of several micrometers and capillary growth with an increase in volume during retraction. This is thought to be a consequence of nanobubbles resting on top of the surface features and an influx of air from the crevices between the particles on the surface.

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Nanomechanical mapping of a high curvature polymer brush grafted from a rigid nanoparticle

Analysis of interaction forces when probing a silica core-polyelectrolyte brush shell nanoparticle, adsorbed on a silica substrate and bathed by aqueous electrolyte solution, with an ultrasharp atomic force microscopy (AFM) tip provides a spatially resolved map of heterogeneous mechanical properties across the nanoparticle. The deformation of the brush is mainly compressive when probed directly above the nanoparticle centre and mainly deflective when probed at a finite horizontal distance away from the centre. The brush is significantly stiffer against compression than against deflection, and ionization of the brush has a greater stiffening effect against compression than deflection. Whereas a height image of the core-shell nanoparticle was unremarkable, showing a monotonic decrease in height with increasing horizontal distance.
from the centre, brush deformation, energy dissipation and adhesion displayed local minima over the centre and maxima at a finite horizontal distance away from the centre, corresponding to a position near the rigid core nanoparticle edge. The different response to brush deformation depending on the angle of probing is relevant to the interactions of brush-decorated macroscopic surfaces with submicrometer roughness and to the interactions of brush-decorated nanoparticles with ultrafine structures in their environments. © 2012 The Royal Society of Chemistry.

On understanding of the Hofmeister effect: How addition of salt alters the stability of temperature responsive polymers in aqueous solutions

In the present study, differential scanning calorimetry was employed to investigate the temperature induced phase separation process of poly(propylene oxide) in a pure aqueous solution and in the presence of five different potassium salts at three different concentrations. The different salts affected the phase separation temperature in accordance with the Hofmeister series with the three salts, KF, KCl and KBr, inducing a clear salting-out effect, one salt, KSCN, inducing a clear salting-in effect and one borderline salt, KI, showing a salting-in or a salting-out effect depending on the salt concentration. It was further observed that the phase separation enthalpy was almost unaffected by the presence of KF, KCl, KBr and KI, while the presence of KSCN led to a significant decrease in this quantity. This suggests that KF, KCl, KBr and KI have a very moderate influence on the PPO hydration, while KSCN appears to decrease the hydrophobic hydration of the PPO chains. The order of how the salts affect the phase separation temperature is in agreement with data for the partition coefficients of the anions between bulk water and at the air-water interface, but only partially in agreement with data related to ion hydration and water structuring effects. These observations are discussed in relation to existing models of how the different nature of the ion and polymer hydration can lead to effective attractive and repulsive ion-polymer interactions depending of the exact chemistry of the ions and the polymer. It is suggested that the previous confusion about the Hofmeister effect is due to a misleading conceptual picture of how polymer hydration is affected by the presence of ions. It is concluded that the Hofmeister effects, in the present case, can be described by a balance between the effective interactions governed by the asymmetric hydration of ions and hydrophobic polymers. This journal is © 2012 The Royal Society of Chemistry.
Structural and Nanomechanical Properties of Paperboard Coatings Studied by Peak Force Tapping Atomic Force Microscopy

Paper coating formulations containing starch, latex, and clay were applied to paperboard and have been investigated by scanning electron microscopy and Peak Force tapping atomic force microscopy. A special focus has been on the measurement of the variation of the surface topography and surface material properties with a nanometer scaled spatial resolution. The effects of coating composition and drying conditions were investigated. It is concluded that the air-coating interface of the coating is dominated by close-packed latex particles embedded in a starch matrix and that the spatial distribution of the different components in the coating can be identified due to their variation in material properties. Drying the coating at an elevated temperature compared to room temperature changes the surface morphology and the surface material properties due to partial film formation of latex. However, it is evident that the chosen elevated drying temperature and exposure time is insufficient to ensure complete film formation of the latex which in an end application will be needed.

Temperature-Dependent Competition between Adsorption and Aggregation of a Cellulose Ether - Simultaneous Use of Optical and Acoustical Techniques for Investigating Surface Properties

Adsorption of the temperature-responsive polymer hydroxypropylmethylcellulose (HPMC) from an aqueous solution onto hydrophobized silica was followed well above the bulk instability temperature (T2) in temperature cycle experiments. Two complementary techniques, QCM-D and ellipsometry, were utilized simultaneously to probe the same substrate immersed in polymer solution. The interfacial processes were correlated with changes in polymer aggregation and viscosity of polymer solutions, as monitored by light scattering and rheological measurements. The simultaneous use of ellipsometry...
and QCM-D, and the possibility to follow layer properties up to 80 °C, well above the T2 temperature, are both novel developments. A moderate increase in adsorbed amount with temperature was found below T2, whereas a significant increase in the adsorbed mass and changes in layer properties were observed around the T2 temperature where the bulk viscosity increases significantly. Thus, there is a clear correlation between transition temperatures in the adsorbed layer and in bulk solution, and we discuss this in relation to a newly proposed model that considers competition between aggregation and adsorption/deposition. A much larger temperature response above the T2 temperature was found for adsorbed layers of HPMC than for layers of methyl cellulose. Possible reasons for this are discussed.

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Amontonian frictional behaviour of nanostructured surfaces
With nanotextured surfaces and interfaces increasingly being encountered in technological and biomedical applications, there is a need for a better understanding of frictional properties involving such surfaces. Here we report friction measurements of several nanostructured surfaces using an Atomic Force Microscope (AFM). These nanostructured surfaces provide well defined model systems on which we have tested the applicability of Amontons' laws of friction. Our results show that Amontonian behaviour is observed with each of the surfaces studied. However, no correlation has been found between measured friction and various surface roughness parameters such as average surface roughness (Ra) and root mean squared (rms) roughness. Instead, we propose that the friction coefficient may be decomposed into two contributions, i.e., \( \mu = \mu + \mu_g \), with the intrinsic friction coefficient \( \mu \) accounting for the chemical nature of the surfaces and the geometric friction coefficient \( \mu_g \) for the presence of nanotextures. We have found a possible correlation between \( \mu_g \) and the average local slope of the surface nanotextures.

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Amontonian Friction Induced by Flexible Surface Features on Microstructured Silicon

Friction between nonadhering sliding surfaces are normally described by Amontons’ law, which states that there exists a linear relationship between the friction force and the normal applied load and that the friction force is independent of the macroscopic contact area between the surfaces and the sliding velocity. In this study we have measured friction as a function of applied load between a spherical silica particle and a microstructured silicon surface consisting of arrays of vertical microneedles, and we have challenged Amontons’ law by changing the size of the silica particle and the sliding velocity. First, when looking at the friction as a function of time for a given applied load, the friction force was observed to oscillate with a period related to the spacing between the microneedles when using a small silica particle, whereas the friction force exhibited a more random variation when a larger silica particle was used. The oscillation in the friction force is a direct evidence for bending and release of individual microneedles and the observation illustrates that the energy dissipating mechanism becomes hidden in the friction data when the dimensions of the sliding body becomes much larger than the length scale of the surface features causing the friction. Second, when looking at the average friction force as a function of applied load we find, in accordance with Amontons’ law, a linear relationship between the friction force and the applied load and the friction force is independent of both the size of the sliding silica particle and of the sliding velocity. One exception from this, however, was observed when sliding a small silica particle at low velocity, where a deviation from Amontons’ law was noticed. The deviation from Amontons’ law is suggested to be attributed to a change in the energy dissipating mechanism giving rise to the friction force. In light of that it is suggested that Amontons’ law only is valid as long as the main energy dissipating mechanism does not change with the applied load. To get a better understanding of the general validity of Amontons’ law, our results were evaluated against different microscopic models.

Interfacial properties and applications of polymer-grafted nanoparticles

The development of "grafting from" methods of brush formation by polymn. from surface-bound initiators makes it possible to create brush-decorated nanoparticles with large grafting densities. Such particles have proven to be effective emulsifying agents by virtue of their high affinity adsorption to oil/water interfaces. Also, adsorbing brush-grafted nanoparticles as brush building blocks potentially can be used to create a brush-like coating on a larger surface. This presentation will focus on silica nanoparticles with poly(dimethylamino ethylmethacrylate) brushes. The interfacial
properties of these particles, at oil/water, air/water, or silica/water interfaces, depend on the grafting densities and solution conditions that affect brush ionization and long-range colloidal forces. The interfacial tension and Gibbs elasticity of particle monolayers on fluid interfaces will be discussed in connection with Pickering emulsion applications, and adsorption isotherms, layer organization, normal forces and lateral forces on solid surfaces will be discussed with application to tribology.

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**Layer-by-Layer Assemblies of Chitosan and Heparin: Effect of Solution Ionic Strength and pH**

The growth of polysaccharide multilayers consisting of positively charged chitosan (CH) and negatively charged heparin (HEP) was monitored in situ by employing a quartz crystal microbalance (QCM-D) and dual-polarization interferometry (DPI). The main focus was on how the physicochemical properties of the solution affect the growth and structure of the resulting multilayer film. These results showed that when increasing the ionic strength of the polysaccharide solutions at a fixed pH, both the “dry” (optical) (DPI) mass and wet (QCM) mass of the adsorbed multilayer film increased. The same effect was found when increasing the pH while keeping the ionic strength constant. Furthermore, the growth of multilayers showed an exponential-like behavior independent of the solution conditions that were used in this study. It was also established that chitosan was the predominant species present in the chitosan–heparin multilayer film. We discuss the viscoelastic properties of the adsorbed layers and their variation during the multilayer buildup. Interestingly and contrary to common interpretation of the QCM-D results, we found that under one particular solution condition (pH 4.2 and 30 mM NaCl) the increase in the dissipation of oscillation energy from the adsorbed layer was a consequence of layer stiffening rather than indicating a more hydrated and viscous film. On the basis of the widely used Voigt viscoelastic model for an adsorbed layer, we show that it is the film viscosity and shear that define the layer viscoelasticity (structure) of the film and not the absolute value of energy dissipation, which in fact can be very misleading.

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Robust Hydrophobic Surfaces Displaying Different Surface Roughness Scales While Maintaining the Same Wettability

A range of surfaces coated with spherical silica particles, covering the size range from nanometer to micrometer, have been produced using Langmuir–Blodgett (LB) deposition. The particles were characterized both in suspension and in the Langmuir trough to optimize the surface preparation procedure. By limiting the particle aggregation and surface layer failures during the preparation steps, well-defined monolayers with a close-packed structure have been obtained for all particle sizes. Thus, this procedure led to structured surfaces with a characteristic variation in the amplitude and spatial roughness parameters. In order to obtain robust surfaces, a sintering protocol and an AFM-based wear test to determine the stability of the deposited surface layer were employed. Hydrophobization of the LB films followed by water contact angle measurements showed, for all tested particle sizes, the same increase in contact angle compared to the contact angle of a flat hydrophobic surface. This indicates nearly hexagonal packing and gives evidence for nearly complete surface wetting of the surface features.

Temperature-dependent adsorption of cellulose ethers on silica and hydrophobized silica immersed in aqueous polymer solution

The influence of temperature on adsorption and the adsorbed layer properties of methylcellulose (MC) and hydroxypropylmethylcellulose (HPMC) were investigated on silica and hydrophobized silica surfaces immersed in aqueous polymer solution. To achieve a concise understanding a quartz crystal microbalance with dissipation, ellipsometry, and atomic force microscopy imaging were employed. These techniques provide complementary information on the structure, mass and viscoelastic properties of the polymer layers. Adsorption was first allowed at 25°C. Next, the temperature was increased step-wise up to 50°C and then decreased again. This procedure highlights the temperature dependence of the adsorbed material, as well as the hysteresis in the adsorption due to temperature cycling. A change in temperature not only affects the adsorbed amount, but also the properties of the layer as illustrated by measurements of its water content, thickness and viscoelasticity. © The Royal Society of Chemistry 2011.
Temperature responsive surface layers of modified celluloses

The temperature-dependent properties of pre-adsorbed layers of methylcellulose (MC) and hydroxypropylmethylcellulose (HPMC) were investigated on silica and hydrophobized silica surfaces. Three different techniques, quartz crystal microbalance with dissipation monitoring, ellipsometry, and atomic force microscopy imaging, were used, providing complementary and concise information on the structure, mass and viscoelastic properties of the polymer layer. Adsorption was conducted at 25 °C, followed by a rinsing step. The properties of such pre-adsorbed layers were determined as a function of temperature in the range 25 °C to 50 °C. It was found that the layers became more compact with increasing temperature and that this effect was reversible, when decreasing the temperature. The compaction was more prominent for MC, as shown in the AFM images and in the thickness data derived from the QCM analysis. This is consistent with the fact that the phase transition temperature is lower, in the vicinity of 50 °C, for MC than for HPMC. The water content of the adsorbed layers was found to be high, even at the highest temperature, 50 °C, explored in this investigation.

Toward Homogeneous Nanostructured Polymeric/Resin Blends

The high interest in applications of conducting polymers, especially polyaniline (PANI), makes it important to overcome limitations for effective usage due to poor processability and solubility. One promising approach is to make blends of PANI in polymeric resins. However, in this approach other problems related to the difficulty of achieving a homogeneous PANI dispersion arise. The present article is focused on this general problem, and we discuss how the synthesis method, choice of dopant and solvent as well as interfacial energies influence the dispersibility. For this purpose, different synthesis methods and dopants have been employed to prepare nanostructures of polyaniline. Dynamic light scattering analysis of dispersions of the synthesized particles in several solvents was employed in order to understand how the choice of solvent affects PANI aggregation. Further information on this subject was achieved by scanning electron microscopy studies of PANI powders dried from various solutions. On the basis of these results, acetone was found to be a suitable dispersion medium for PANI. The polymer matrix used to make the blends in this work is a UV-curing solvent-free resin. Therefore, there is no low molecular weight liquid in the system to facilitate the mixing process and promote formation of homogeneous dispersions. Thus, a good compatibility of the components becomes crucial. For this reason, surface tension and contact angle measurements were utilized for characterizing the surface energy of the PANI particles and the polyester acrylate (PEA) resin, and also for calculating the interfacial energy between these two components that revealed
good compatibility within the PANI/PEA blend. A novel technique, based on centrifugal sedimentation analysis, was employed in order to determine the PANI particle size in PEA resin, and high dispersion stability of the PANI/PEA blends was suggested by evaluation of the sedimentation data.

Confinement of linear polymers, surfactants, and particles between interfaces
The review addresses the effect of geometrical confinement on the structure formation of colloidal dispersions like particle suspensions, (non)micellar surfactant solutions, polyelectrolyte solutions and mixed dispersions. The dispersions are entrapped either between two fluid interfaces (foam film) in a Thin Film Pressure Balance (TFPB) or between two solid interfaces in a Colloidal Probe Atomic Force Microscope (Colloidal Probe AFM) or a Surface Force Apparatus (SFA). The oscillating concentration profile in front of the surface leads to an oscillating force during film thinning. It is shown that the characteristic lengths like the distance between particles, the distance between micelles, or the mesh size of the polymer network remain the same during the confining process. The influence of different parameters like ionic strength, molecular structure, and the properties of the outer surfaces on the structure formation are reported. The confinement of mixed dispersions might lead to phase separation and capillary condensation, which in turn causes a pronounced attraction between the two opposing film surfaces.

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Confinement of linear polymers, surfactants, and particles between interfaces
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Effect of local curvature on the interaction between hydrophobic surfaces

Surface structure, including roughness and chemical heterogeneities, is known to be of importance for the surface interaction forces observed between hydrophobic and superhydrophobic surfaces. In this study, silica particles have been used to prepare structured particulated surfaces with a controlled roughness using Langmuir-Blodgett deposition or a drop coating technique. The surfaces were characterized by SEM and AFM. The AFM colloidal probe technique was employed for probing the interaction between a micro-size hydrophobic particle and hydrophobic surfaces with a sintered and silanized nano-sized silica particle monolayer. These measurements indicate that the adhesion force is increased by a decrease in particle size. Larger roughness gives larger crevices on the surface and more air/vapor accumulation but the capillary growth is impaired since the three-phase line (solid-liquid-air) has to move over a longer distance with an increase in the size of the surface features.

Friction in aqueous media tuned by temperature-responsive polymer layers

An atomic force microscope colloidal probe technique has been employed to probe normal and friction forces between silica surfaces coated with adsorbed layers of a diblock copolymer of the composition poly(N-isopropylacrylamide) 48-block-poly(3-acrylamidopropyl)trimethylammonium chloride) 20, abbreviated PNIPAAM48-b-PAMPTMA(+)20. The interactions between the PNIPAAM48-b-PAMPTMA(+)20-coated surfaces across a 0.1 mM NaCl (pH 6) solution at 25 °C are purely repulsive, due to a combination of steric and electrostatic double-layer forces. However, when the temperature is increased to 35 °C, and subsequently to 45 °C, an attractive force develops at short separations due to the unfavourable PNIPAAM-water interaction at these temperatures. The temperature-dependent polymer-water interaction has implications for the friction force between the layers. At 25 °C a frictional force that increases linearly with increasing load is observed once the surfaces are brought into close contact. At higher temperatures significantly higher friction forces appear as a consequence of attractive segment-segment interactions. Further, a clearly expressed hysteresis between friction forces encountered on loading and unloading is detected. Our results demonstrate that both normal and friction forces between surfaces can be controlled by temperature changes when temperature-responsive polymers are employed, and friction forces can be adjusted as required from low to high. © 2010 The Royal Society of Chemistry.
Letter to the Editor: Friction between Surfaces - Polyacrylic Acid Brush and Silica - Mediated by Calcium Ions
With this letter, we report how friction can be controlled by inducing physical bonds solely within a polyelectrolyte brush layer, while keeping repulsive interactions between the brush layer and the bare surface that slides above. Our results imply that the nature of the bare surface is of minor importance as long as the repulsive surface interaction is maintained. © Taylor & Francis Group, LLC.

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Probing material properties of polymeric surface layers with tapping mode AFM: Which cantilever spring constant, tapping amplitude and amplitude set point gives good image contrast and minimal surface damage?
A phase shift between the oscillatory motion and drive motion of an AFM-cantilever used for tapping mode AFM imaging can be related to adhesive and elastic properties of surface layers. In this study it was studied how optimal contrast between hard and soft surface layers can be achieved while minimizing the surface damage. This was investigated by performing classical force-distance measurements while driving the cantilever as in tapping mode imaging. The amplitude and phase response as a function of the average tip-surface separation was recorded. Five different cantilevers with a wide range of spring constants and four different tapping amplitudes were investigated and compared. Based on these experiments it is concluded that too stiff cantilever, high free tapping amplitude and low amplitude set point value often lead to surface damage, while too low spring constant and low free tapping amplitude result in poor phase image contrast. Intermediate values where little surface damage and significant image contrast are obtained were identified. In all cases it was observed that the best image contrast was obtained when the amplitude set point was chosen such that the amplitude during imaging was reduced to approximately 50% of the free amplitude.
Protein interactions with bottle-brush polymer layers: Effect of side chain and charge density ratio probed by QCM-D and AFM

Silica surfaces were coated with a range of cationic bottle-brush polymers with 45 units long poly(ethylene oxide) side chains, and their efficiency in reducing protein adsorption was probed by QCM-D, reflectometry and AFM. Preadsorbed layers formed by bottle-brush polymers with different side chain to charge ratio was exposed to two proteins with different net charge, lysozyme and BSA. The reduction in protein adsorption was found to depend on both the type of protein and on the nature of the polyelectrolyte layer. The most pronounced reduction in protein adsorption was achieved when the fraction of charged backbone segments was in the range 0.25–0.5 equivalent to a fraction of poly(ethylene oxide) side chains of 0.75–0.5. It was concluded that these polymers have enough electrostatic attachment points to ensure a strong binding to the surface, and at the same time a sufficient amount of poly(ethylene oxide) side chains to counteract protein adsorption. In contrast, a layer formed by a highly charged polyelectrolyte without side chains was unable to resists protein adsorption. On such a layer the adsorption of negatively charged BSA was strongly enhanced, and positively charged lysozyme adsorbed to a similar extent as to bare silica. AFM colloidal probe force measurement between silica surfaces with preadsorbed layers of bottle-brush polymers were conducted before and after exposure to BSA and lysozyme to gain insight into how proteins were incorporated in the bottle-brush polymer layers.
Tuning structural forces between silica surfaces by temperature-induced micellization of responsive block copolymers

The aim of this study is to demonstrate a method to control interactions between two surfaces by the use of a responsive solution. This was done by performing AFM-based force measurements between two silica surfaces immersed in an aqueous solution of thermo-responsive Pluronics P85 block copolymers. For this system we demonstrate that one can switch between a situation where no long-range forces are acting between the surfaces to a situation where a long-range structural force, oscillating between attractive and repulsive force regimes, is controlling the surface interaction. This shift in behavior is caused by a long-range order introduced by temperature-induced micellization of the block copolymers and is thus simply achieved by changing the temperature from below to above the micellization temperature. We propose that the use of micelle-forming responsive block copolymers is a general method for reversibly controlling surface interactions by a temperature switch. Since the force control is achieved by changes occurring in bulk solution, the nature of the surfaces is expected to play only a relative minor role.

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Force Pulling of Single Cellulose Chains at the Crystalline Cellulose−Liquid Interface: A Molecular Dynamics Study
Pulling single cellulose molecules from a crystalline cellulose surface has been modeled by molecular dynamics (MD) simulations of the experimental procedure used in atomic force microscopy (AFM). Specifically, the aim of the study was to investigate cellulose interactions at desorption. Simulations were performed in both water and the organic solvent cyclohexane. Moreover, the effects of initial octamer conformation and orientation with respect to the surface chains were studied. A strong effect from the solvent was observed. In cyclohexane, normal forces of 200–500 pN and energies of 43.5 ± 6.0 kJ/mol glucose unit were required to pull off the octamer. The normal forces in water were substantially lower, around 58 pN, and the energies were 18.2 ± 3.6 kJ/mol glucose unit. In addition, the lateral components of the pull-off force were shown to provide information on initial conformation and orientation. Hydrogen bonds between the octamer and surface were analyzed and found to be an important factor in the pull-off behavior. Altogether, it was shown that MD provides detailed information on the desorption processes that may be useful for the interpretation of AFM experiments.

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How to measure forces with atomic force microscopy without significant influence from nonlinear optical lever sensitivity

In an atomic force microscope AFM, the force is normally sensed by measuring the deflection of a cantilever by an optical lever technique. Experimental results show a nonlinear relationship between the detected signal and the actual deflection of the cantilever, which is widely ignored in literature. In this study we have designed experiments to investigate different possible reasons for this nonlinearity and compared the experimental findings with calculations. It is commonly assumed that this nonlinearity only causes problems for extremely large cantilever deflections. However, our results show that the nonlinear detector response might influence many AFM studies where soft or short cantilevers are used. Based on our analysis we draw conclusions of the main reason for the nonlinearity and suggest a rule of thumb for which cantilevers one should use under different experimental conditions. © 2009 American Institute of Physics.

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Kraften mellem to molekyler kan nu måles

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Force trace hysteresis and temperature dependence of bridging nanobubble induced forces between hydrophobic surfaces

An atomic force microscope and the colloidal probe technique are used to probe the interaction between a hydrophobic particle and a hydrophobic surface in water. The characteristics of the observed force curves strongly suggest that a gas bubble is formed when the particle is moved toward the surface and that the bubble ruptures when the particle subsequently is retracted from the surface. We demonstrate that this type of interaction is not unique for hydrophobic surfaces in water since the interaction between hydrophilic surfaces in air provides very similar force curves. However, the interaction between hydrophobic surfaces vanish if water is replaced by an organic solvent with low polarity. The bridging bubble model is employed to explain the hysteresis observed between approach and retraction force traces and experimental conditions where the hysteresis can be almost eliminated are identified. Finally, it is demonstrated that the hydrophobic interaction is strongly temperature dependent and this dependence can be attributed mainly to the decreasing solubility of air in water with increasing temperature. © 2008 American Chemical Society.

Interactions between a Polystyrene Particle and Hydrophilic and Hydrophobic Surfaces in Aqueous Solutions

Abstract: The interaction between a colloidal polystyrene particle mounted on an AFM cantilever and a hydrophilic and a hydrophobic surface in aqueous solution is investigated. Despite the apparent simplicity of these two types of systems a variety of different types of interactions are observed. The system containing the polystyrene particle and a hydrophilic surface shows DLVO-like interactions characteristic of forces between charged surfaces. However, when the surface is hydrophobized the interaction changes dramatically and shows evidence of a bridging air bubble being formed between the particle and the surface. For both sets of systems, plateaus of constant force in the force curves are obtained when the particle is retracted from the surface after being in contact. These events are interpreted as a number of individual polystyrene molecules that are bridging the polystyrene particle and the surface. The plateaus of constant force are expected for pulling a hydrophobic polymer in a bad (hydrophilic) solvent. The plateau heights are found to be of uniform spacing and independent of the type of surface, which suggests a model by which collapsed polymers are extended into
the aqueous medium. This model is supported by a full stretching curve showing also the backbone elasticity and a stretching curve obtained in pentanol, where the plateau changes to a nonlinear force response, which is typical for a polymer in a good or neutral solvent. We suggest that these polymer bridges are important in particular for the interaction between polystyrene and the hydrophilic surface, where they to some extent counteract the long-range electrostatic repulsion.

**Dynamic Strength of the Interaction between Lung Surfactant Protein D (SP-D) and Saccharide Ligands**

In order to investigate the dynamic strength of the interaction between lung surfactant protein D (SP-D) and different sugars, maltose, mannose, glucose, and galactose, we have used an atomic force microscope to monitor the interaction on a single molecule scale. The experiment is performed by measuring the rupture force when the SP-D - sugar bond is subjected to a continuously increasing force. Under these dynamic conditions, SP-D binds strongest to D -mannose and weakest to maltose and D -galactose. These results differ from equilibrium measurements wherein SP-D exhibits preference for maltose. On the basis of this finding, we propose that the binding of the disaccharide maltose to SP-D, which is energetically stronger than the binding of any of the monosaccharides, alters the structure of the binding site in a way that lowers the dynamic strength of the bond. We conclude that determining the strength of a protein - ligand bond under dynamic stress using an atomic force microscope is possibly more relevant for mimicking the actual nonequilibrium physiological situation in the lungs.
Ligand-receptor interactions and membrane structure investigated by AFM and time-resolved fluorescence microscopy

The atomic force microscope (AFM) and the associated dynamic force spectroscopy technique have been exploited to quantitatively assess the interaction between proteins and their binding to specific ligands and membrane surfaces. In particular, we have studied the specific interaction between lung surfactant protein D and various carbohydrates. In addition, we have used scanning AFM and time-resolved fluorescence microscopy to image the lateral structure of different lipid bilayers and their morphological changes as a function of time. The various systems studied illustrate the potential of modern AFM techniques for application to biomedical research, specifically within immunology and liposome-based drug delivery. Copyright (c) 2007 John Wiley & Sons, Ltd.

Dynamic force spectroscopy on soft molecular systems: Improved analysis of unbinding spectra with varying linker compliance

Dynamic force spectroscopy makes it possible to measure the breaking of single molecular bonds or the unfolding of single molecules subjected to a time-dependent pulling force. The force needed to break a single bond or to unfold a domain in a protein depends critically on the time dependence of the applied force. In this way the elastic response couples to the unbinding force. We have performed an experimental and theoretical examination of this coupling by studying the well-known biotin–streptavidin bond in systems incorporating two common types of linkers. In the first case biotin is linked by bovine serum albumin (BSA) and it is observed that this linker has a linear elastic response. More surprisingly we find that its force constant varies significantly between repeated force curves. It is demonstrated that by sorting the force curves according to the force constant of the linker we can improve the data analysis and obtain a better agreement between experimental data and theory. In the second case biotin is linked by poly(ethylene glycol) (PEG), which has a soft nonlinear elastic response. A numerical calculation of the unbinding statistics for the polymer system agrees quantitatively with experiments. It demonstrates a clear decrease in unbinding forces resulting from the polymer linker.
Experimental studies of the dynamic mechanical response of a single polymer chain

The high-frequency and low-amplitude dynamic mechanical response from a single poly(vinyl alcohol) chain was investigated. Modification of a commercial atomic force microscope enabled high-frequency and low-amplitude periodic deformations of polymer chains during extension to be performed. Such an experiment has previously been considered untenable due to hydrodynamic and viscous effects, but we introduce here a method to isolate the response of the polymer from the hydrodynamic response. For periodic deformations with frequencies of 400-2000 Hz and amplitudes of 0.55-16.9 nm, we find that the dynamic mechanical response from poly(vinyl alcohol) does not differ from its static response. This result is not unexpected as poly(vinyl alcohol) is a highly flexible polymer with intramolecular relaxation processes taking place on a short time scale. The choice of a polymer with a fast relaxation allows its static properties to be recovered from the dynamic measurements and enables the method suggested in this paper for decoupling the polymer response from the hydrodynamic response to be validated.