POSTER SESSION

Bridging Nanoscale Forces and Interfacial Phenomena with the Macroscopic World

Chair: Professor Suzanne Giasson
co-Chair: Professor Norma Alcantar

P1

New Optical Methods In-Situ of the eSFA

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The surface forces apparatus (SFA) is a well-established tool to study the physical properties of confined fluids. Confinement is realized between two atomically smooth mica sheets, silvered on the backside and mounted on two silica supports in a crossed cylinder arrangement. The surface separation is measured locally at the point of closest approach by analysis of the white light interference spectrum transmitted through the thin-film interferometer. For dynamic experiments e.g. squeeze-out of confined fluids or lubrication with molecularly thin films, it is of great interest to image the entire contact area in real-time. We present a novel concept – Optical spectral correlation (OSC) – that uses light transmitted through the thin-film interferometer and analyzes it with a dedicated optical correlator. The correlated light is detected with a CCD camera, yielding a laterally resolved, real-time correlation map. The intensity information can then be readily transformed into physical quantities, such as surface separation and/or local refractive index of the confined film. A simultaneous distance measurement using the conventional Fast Spectral Correlation (FSC) method allows an online calibration of the OSC map. The nominal distance resolution of OSC is limited by the noise of the detected CCD signal, mainly inevitable shot noise. We discuss the requirements of the CCD camera and demonstrate that we can achieve subÅ-resolution in single frame images at sample rates of up to several tens of hertz. In combination with newly developed substrate holders – generating large area contacts with diameters of several hundreds of microns – OSC becomes a powerful tool to study confined fluid films. We present first data showing new aspects of the behavior and the dynamics of such systems.

P2

Adhesion and Stress Relaxation in Living Cells

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Interaction of living cells with a substrate is becoming an important field of research for the scientific community. Cell/surface interactions are known to induce very different responses from cells as apoptosis or active division [1] as well as to affect their rheological properties [2,3]. A precise knowledge of these interactions and their impact on cell behavior is still a challenge because of the variety of their manifestations. We choose to use SFA technique to correlate cell mechanical behavior to their adhesion properties with different model substrates. Living cells were seeded on treated mica surfaces and compression force profiles were performed at 37.2 °C. Mica was functionalized with different self-adsorbed or grafted polymers. Stress relaxation in the cell monolayer was monitored in the decompression force profile by following fringes displacement with time. Data were fitted to several mechanical models in order to extract rheological properties and to compare them with available published data. Preliminary results show a strong dependence of stress relaxation time of the cells with applied force. Influence of substrate will also be discussed.

[1] D.E. Ingber, PNAS 100 (2003) 1472–1474.

[2] N. Desprat, Biophys J 88 (2005) 2224.

[3] M. Puig-de-Morales, E. Millet, B. Fabry, D. Navajas, N. Wang, J.P. Butler, J.J. Fredberg, Am J Physiol: Cell Physiol 287 (2004) 643.

P3

Hairy and Slippery: Surface Forces and Friction between Surface-Grown Polymer Brushes in Aqueous Media

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Interactions (surface forces and friction) between surfaces at close proximity in aqueous media are important in many technological applications and biological processes. Polymers may be readily anchored on the surface to tailor these interactions, and an effective such strategy is to formulate polymer brushes on the surface. Most often, this is achieved with a "grafting-to" approach, i.e., end adsorbing a polymer to a solid surface. A recent alternative approach is "grafting-from", i.e., directly growing polymers from a substrate. Using a version of the surface force apparatus, we have measured surface forces and friction between two mica surfaces in aqueous media where such possible different approaches are explored. Our results show that grafting densities of surface-grown polymer brushes attained may indeed be substantially higher than achievable using classical physic-grafting methods. We will discuss the possible implications of our results to the biolubrication process, in which biopolymers end anchored on cell surfaces through trans-membrane proteins facilitate frictionless sliding between biological tissues.

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P4

Surface Interactions and Conformations of Adsorbed Alpha Helices

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Interaction between amphiphilic α-helical proteins (human apolipoprotein AII) adsorbed on a hydrophilic surface from a buffer solution at pH 4 was studied, using an interferometric surface force apparatus. The interaction forces between the adsorbed layers of α-helices are mainly composed of electrostatic double layer forces at large surface distances and of steric repulsive forces at small distances. Amphiphilicity of the α-helix structure facilitates the formation of protein multilayers next to the surfaces. We also found that the interaction mica-protein is stronger than protein-protein interaction. The results of protein adsorption and force interaction suggest that they are consequences of the protein secondary structure, the amphiphilic α-helix motif.

P5

Novel Polymer-Metal Nano-Composites for Applications in Detection and Sensing

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Detection of trace elements such as organic contaminants, explosive residues, and metal ions is an intellectually challenging task in science and engineering. It is also a topic of increasing importance due to its impact on the society and the environment. "Stimuli-sensitive" materials are ideal candidates for sensors as they are able to respond to changes in their environment and these responses can be transduced into measurable signals. The purpose of the research in this project is to combine organic polymers with inorganic constituents to tailor the binding properties and the responses of the "composite" material for detection of metals ions in aqueous solutions.

In this project, we focus on a thermally responsive polymer such as poly(N-isopropylacrylamide) (PNIPAM), which exhibits a well-known reversible coil to globule transition in aqueous media with changes in temperature. We are combining cross-linked microgels formed from copolymers of PNIPAM with gold nanoparticles (GNP). By using functional groups in the copolymers as potential sites for binding metal ions and use of imprinting techniques, we aim to explore the composite properties to sense the presence of metal ions in solution. The poster presentation will discuss our experimental approach, results of ongoing work, and future directions.

P6

The Effect of Wettability on Capillary Condensation of Liquid below the Melting Point

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Adsorption and capillary condensation of cyclooctane below its bulk melting point T_m (14 °C) have been studied with a surface force apparatus (SFA). Comparisons were made between bare mica surfaces and fluorocarbon surfaces prepared by adsorbing heptadecafluorodecylpyridinium chloride to mica. As with previously investigated alcohols (*tert*-butanol, *neo*-pentanol, menthol), the capillary condensates remain liquid below the melting point, and their size is inversely proportional to the temperature below T_m. These SFA experiments thus probe melting-point depression in confinement, using a single pore of variable dimension, and the two different surfaces are equivalent to different pore wettabilities. The condensates formed between the fluorocarbon surfaces are smaller those between the mica surfaces. With both surfaces, however, the relationship between the condensate size and the solid-liquid interfacial energy of the condensing substance is different to what was found with the alcohols. The results are discussed in view of the larger contact angle (~ 45°) of liquid cyclooctane on the fluorocarbon surface compared to mica (< 10°), and other differences in the wetting behaviour of both solid and liquid cyclooctane on the two surfaces.

P7

Investigating Slip Boundary Conditions with Squeeze Film Measurements in the SFA and AFM

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According to the no-slip boundary condition of hydrodynamics, the flow velocity of a liquid at a solid-liquid interface is equal to the velocity of the solid. The general acceptance of the validity of the no-slip theory for Newtonian liquids is based on experimental observations, rather than on any fundamental theory. In recent years, with the improvement of fine-scale experimental techniques, questions have been raised about the universality of this boundary condition, and whether in some situations the velocity-matching condition should be applied not at the interface but some distance to the solid side of it. This would correspond to the liquid slipping over the solid surface, and the distance between the interface and the (virtual) position of the velocity match defines the ‘slip length’, which is used to characterize the amount of slip. A better understanding of hydrodynamic boundary conditions is important to the study of liquid flow in confined spaces.

The flow of simple liquids in a confined geometry has been studied by means of *squeeze film* experiments, using the surface force apparatus (SFA) and more recently, using the colloid-probe atomic force microscope (AFM). These experiments consist of a thin liquid film confined between two solid surfaces that can be driven up and down relative to one another in a direction normal to both surfaces. In the current project, we investigate and compare the two aforementioned techniques for studying the boundary conditions in the squeeze film geometry, both from an experimental viewpoint and by examining the data analysis and interpretation methods employed. In particular, we present an alternative method of analysis that avoids the subjective judgments required to derive force curves from AFM data (e.g. locating the constant compliance region accurately).

P8

Polymeric Micelles as Soft Colloids: How Far Can We Push the Analogy?

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In water the symmetric triblock copolymer F68, $(PEO)_{76}(PPO)_{29}(PEO)_{76}$ forms spherical micelles upon heating. This intriguing behaviour is used on large scale in industry. But also scientifically this polymeric surfactant is of intrest, as the micelles can, under given conditions, crystallize and behave like hard colloidal solutions. Here we report an experimental study of the phase diagram, rheology and dynamics of the symmetric triblock copolymer F68 in water in the presence of sodium chloride. At high temperatures and high polymer concentrations, this system forms a crystal consisting of micelles with an aggregation number of 10-15. The presence of salt qualitatively changes the phase diagram, as it induces a cloud point that is not found in salt-free, aqueous solutions. The appearance of a cloud point inside the 2-phase region is indicative for short ranged attractive interactions between the micelles. This finding is surprising inasmuch as such a liquid-to-liquid phase transition is often obstructed by gelation and thus rarely observed. Above the cloud point the solution becomes unstable and separates into a polymer rich and a polymer poor phase. The aggregation number of the aggregates in the polymer rich phase increases dramatically.

KEYWORDS: Micelles, short-ranged interactions, cloud point, salt effect.

P9

Novel Polymer-Metal Nano-Composites for Applications in Detection and Sensing

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We find that the static structure of charged liposome dispersions, independently of the interaction potential determining it, governs the short- time dynamics in these systems. By light scattering we find evidence of an effective interaction that is not purely repulsive. Existent hydrodynamic models are still able to predict the short-time dynamics of liposomes in suspension when the measured static structure factor is used as input in the calculations. Our results suggest the generality of these theories, which to our knowledge have been only tested in pure repulsive systems.

P10

The Complex Influence of Electrolytes on Bubble Coalescence

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At high concentrations of electrolytes the double layer interaction is screened and short range forces determine colloidal behavior. Consequently the type of ions that are in solution becomes all important and interactions become considerably more complex. In a sense there is a transition from a physics regime (where ions are treated as point charges) to a chemistry regime where the precise character (charge, size, polarisability etc) and pairing of ions is important. Such complexity is exploited universally in nature where it is commonly recognised that ion-specificity is commonplace. It remains a great challenge for colloid scientists to develop a detailed understanding of ion-specificity. Perhaps the simplest system that reveals such complex behavior is that of gas bubbles in salty water.

For one hundred years it has been recognized that electrolytes at sufficiently high concentrations can inhibit bubble coalescence, but an understanding of this phenomenon is lacking. Further, some electrolytes have no influence on bubble coalescence. This complex situation has been described using empirical rules by Craig, Ninham and Pashley in the early 1990’s, as set out in the table below. However, an understanding of these rules has not been forthcoming. There have been suggestions that they relate to the influence of ions on surface tension or on gas solubility but the experimental data has not been available to fully test these ideas.

Here we report a considerable volume of work on measurements of surface tension and bubble coalescence of electrolyte solutions, both of single electrolytes and mixed electrolytes performed with the aim of elucidating the nature of specific ion effects in bubble coalescence. This has enabled us to rule out surface tension effects as the mechanism of bubble coalescence inhibition and offers support for a recent suggestion by Marcelja regarding the origin of the combining rules.

Continuation:

Ions		H^+	Mg^{2+}	Na^+	Ca^{2+}	K^+	NH_4^+	Cs^+	Li^+	$(CH_3)_4N^+$	$(CH_3)_3NH^+$	$(CH_3)_2NH_2^+$	$(CH_3)NH_3^+$
Assignment		β	α	α	α	α	α	α	α	β	β	β	β
OH^-	α	✗		✓		✓							
Cl^-	α	✗	✓	✓	✓	✓	✓		✓	✗	✗	✗	✗
Br^-	α	✗		✓		✓		✓					
NO_3^-	α	✗		✓	✓	✓	✓		✓				
ClO_3^-	β			✗									
SO_4^{2-}	α	✗	✓	✓			✓		✓				
ClO_4^-	β	✓	✗	✗			✗						
CH_3COO^-	β	✓	✗	✗		✗	✗	✗		✓			
$(COO)_2^{2-}$	α	✗				✓							
SCN^-	β												
IO_3^-													

✓ **Prevents bubble coalescence**

αα= ✓ ββ= ✓

✗ **No effect on coalescence**

αβ= ✗

The effect of different ion pairs on bubble coalescence. αα and ββ combinations inhibit coalescence, whereas αβ and βα combinations have no effect on bubble coalescence relative to pure water behaviour.

P11

Molecular Interactions at the Interface of Nanoemulsions for Drug Detoxification

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Drug toxicity in humans due to illicit drug use, suicide attempts, or iatrogenic complications represents a major health care problem, both in terms of morbidity and economic cost. Many life-threatening drugs do not have specific pharmacological antidotes to reverse the toxic effects that result when an overdose occurs. Therefore, the development of an effective methodology for the removal of free drug from the blood of an overdosed patient in a timely manner (less than 15 minutes) is critically important. In the past few years, efforts have been underway to utilize nanoparticulate systems to accomplish this task. Nanoemulsions are one of the systems that are currently under investigation. Upon injection of a nanoemulsion in the blood of an overdosed person, the nanoemulsion, having extremely high interfacial area, can effectively adsorb drug molecules, and thereby quickly decrease the concentration of free drug molecules in the blood. However, in order to fully grasp their function as toxicity reversal agents, one must understand the molecular mechanism of drug uptake and be able to determine and manipulate the contributing interfacial forces.

Preliminary results from pH studies have led us to believe that electrostatic forces can play a significant role in adsorption/absorption of drug into the nanoemulsion. Amitriptyline Hydrochloride is an antidepressant and as of yet, there is no efficient method to reverse the effects of an overdose in a patient; therefore it is the target drug for the experiments reported here. Amitriptyline has a pKa of approximately 9.4 so that at physiological pH (~ 7.4), it will be positively charged and can thereby interact through electrostatics with a negatively charged nanoemulsion. These nanoemulsions are composed of Pluronic F127, Ethyl Butyrate, and Sodium Caprylate (which gives the negative charge) and are prepared in Phosphate Buffered Saline. The objective of this study is to develop a better understanding of the important interactions that occur between the microemulsion and the drug.

We have shown, through turbidity analysis experiments, that there is a linear relationship between the Amitriptyline Hydrochloride solubilization capacity of the nanoemulsions and Pluronic surfactant concentration up to a certain Pluronic F127 concentration. Above that critical Pluronic F127 concentration, further titration with Amitriptyline never yields turbidity. We have also seen that turbidity is not observed in systems that do not have sodium caprylate present. Based on these findings we have concluded that at the critical Pluronic concentration, there in no longer any free (unassociated) sodium caprylate molecules in the bulk phase. Therefore, we are able to determine how many molecules of sodium caprylate and amitriptyline are associated with each Pluronic molecule. Each Pluronic F127 molecule can associate with approximately fourteen molecules of sodium caprylate and amitriptyline at the critical concentration (i.e. there appears to be a 1:1 association of sodium caprylate to Amitriptyline). This yields further credence to previous pH studies which showed that electrostatic interactions are important in amitriptyline binding to nanoemulsions produced by Pluronic F127 and fatty acid soap. The findings of this study will provide substantial information regarding the mechanism of reduction of overdosed drugs and will allow us to approximate the uptake capacity of a particular nanoemulsion system.

P12

Study and Evaluation of Adhesion Forces and Chemical Structures Involved in the Aggregation Pathways for Both Amyloid Beta Peptides 40 and 42

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Neuritic plaques in Alzheimer's disease patients are predominantly composed of amyloid beta (Aß) peptides with 40 (Aß$_{40}$) and 42 (Aß$_{42}$) amino acid residues. We have followed the aggregation pathways for both Aß$_{40}$ and Aß$_{42}$ peptides under three different incubation conditions. We have identified three specific conformations of the Aß peptides in the aggregation processes. These three conformations are commonly referred as monomeric, oligomeric and fibrillar (1-3) conformations. We have monitored the chemical structures and adsorption behavior as function of time for the peptides dissolved in different incubation media with Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectroscopy and Atomic Force Microscopy (AFM). Two principal outcomes were obtained. We have first verified the occurrence of different folding pathways for both Aß$_{40}$ and Aß$_{42}$, which revealed that Aß$_{42}$ peptide is most likely to aggregate as fibrillar conformations and with a higher surface adhesion tendency than Aß$_{40}$ peptide. And, secondly, we have linked the surface adhesion mechanisms of Aß peptides molecules with their secondary structure evolution, which is critical for the formation and stability of monomeric, oligomeric, and fibrillar conformations. The final product of this work will guide us in the searching of ways to destabilize β-sheets secondary structures propitious for the formation of large aggregates such as fibrils that are responsible for the appearance of neuritic plaques in Alzheimer's disease.

P13

Studies on the Monolayer Lubrication and Direct Observation of PFPE Lubricant Molecules by Cryogenic non-contact AFM under Ultra-High Vacuum

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Hard discs are the most important memory media for not only computer systems but also music recording media like i-Pod or for image storage media, etc. Memory density of hard disk systems increases rapidly in recent years and with increasing density, the distance between disc surface and head decreases rapidly. The distance becomes now less than 10 nm and the thickness of the surface lubricant layer is requested to be less than one nm. This thickness corresponds to almost a monomolecular layer or less of lubricant molecules. Almost all hard disk systems use a PFPE lubricant, Z-dol (a commercial name of Solvay Solexis) of which molecules have two OH groups at both ends of PFPE chains. Therefore, this PFPE lubricant can form stable insoluble monolayers at the water surface by spreading from a volatile fluoro-solvent solution, and the surface density of lubricant molecules can be controlled by compression of the monolayer with movable barriers. The monolayer can be transferred to a solid substrate surface by the LB technique. In this paper, we report direct observation of PFPE lubricant molecules by using cryogenic AFM under ultra-high vacuum.

A monolayer of molecular weight fractionated Z-dol (M.W. 1920) is transferred to a surface of gold-sputtered mica, hydrophilic silicon wafer and actual magnetic disk surfaces. Non-contact AFM observation was done using JSPM-4500 at very low temperature under ultra-high vacuum. It was made clear that lowering of the sample temperature to below the glass transition temperature of PFPE is essential to observe PFPE lubricant molecules, and the ultra-high vacuum environment is also essential to prevent freezing of water on the sample at the low temperatures. With increasing sample temperature gradually from 90 K, we could observe molecular images of PFPE lubricant molecules up to 132 K. At or above 134 K, however, molecular images disappeared. This means that segmental motions of PFPE chains start above this temperature.

Figure 1 shows a non-contact AFM image of Z-dol 1920 lubricant monolayer on the gold-sputtered mica surface. Image size is 100 x 100 nm2 . Observed particulates are the reversed micelles of Z-dol molecules. On the hydrophilic silicon wafer, we could observe single molecules of Z-dol. On the actual disk surface, however, we also observed the reversed micelles, and they gathered along the ridge structure of the texture of the carbon overcoat of disk surface.

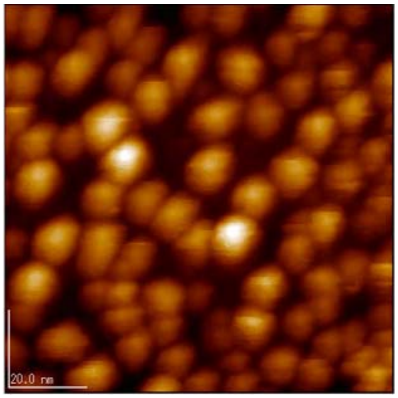

Figure 1, AFM image of Z-dol

P14

Effect of Architecture on the Assembly and Structure of Polymer Brushes

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Polymer brushes are of practical importance because of their ability to straddle phase boundaries and mediate interactions across interfaces. Although a variety of methods exist for tethering polymers to surfaces, one of the most useful methods of creating polymer brushes is via self-assembly of amphiphilic block copolymers. While the structure and properties of linear polymer brushes are well understood, the assembly, structure, and properties of polymer brushes made from branched architectures has not been explored. This presentation will describe our efforts to investigate the impact of chain branching on the self-assembly and structure of polymer brushes made from amphiphilic comb and mikto-arm block copolymers. By monitoring the kinetics of assembly using phase-modulated ellipsometry we find signatures that we attribute to structural reorganizations as the chains become crowded on the surface. Because of increased intramolecular interactions, the equilibrium forces of interaction are also impacted by chain branching. The effect of branching can be incorporated into an Alexander-deGennes type, mean-field model to produce a universal profile that collects the force profiles from brushes of different architecture.

P15

Surface Properties of Charged Polymers Brushes

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Charged polymers at surfaces play a crucial role in designing biomaterials by controlling surface properties and/or functionalizing them. Their role is usually fulfilled by a combination of different types of interaction (electrostatic, steric, hydrophobic, etc). Several experimental and theoretical studies have explored the intrinsic structure and properties of polymer-coated surfaces as a function of grafting density, solvent condition, charge density, ionic strength and pH. The normal and lateral forces between two opposing and moving surfaces bearing different polymers have also been largely investigated. We have shown recently that brushes of charged polymers attached to surfaces rubbing across an aqueous medium exhibit remarkable lubricating properties, even under high compression loads (Nature, 2003, **425**(6954): p. 163-165). However, correlations between molecular conformation of polymer-bearing surfaces and their behaviour are not yet fully understood and are essential for designing biomaterials such as drug delivery systems and wear-resistant implants. To obtain different conformation, we develop a technique to graft different diblocks on surfaces in a control manner.

The approach consists of covalently attaching a thin monolayer of end-functionalized polystyrene (PS) to silica or mica surfaces by adsorption from solution. Then, a PS-b-X diblock copolymer is deposited using the Schaeffer technique (variant of the familiar Langmuir-Blodgett technique). By heating above the T_g and subsequent cooling, the PS blocks of the copolymer diffuse into the end-attached PS monolayer thereby attaching the copolymer onto the surface. We succeeded to build a nice and homogeneous monolayer of PS (with no aggregates and showing no dewetting) on silicon wafers as well as on plasma activated mica surfaces using self-adsorption. AFM revealed wide areas without defects and with a low roughness (RMS $\approx$ 0.2 nm). The surfaces initially hydrophilic ($\theta \approx 0°$) became hydrophobic ($\theta \approx 90°$) and the attachment was irreversible confirming the successful grafting of the polymer. On these PS-coated surfaces, we investigated the behaviour of pH sensitive diblock copolymer, the polystyrene-b-polyacrylic acid (PS-b-PAA). The presence of the grafted diblock on the PS-coated surface was confirmed by contact angle measurements and AFM. The PS surfaces initially hydrophobic became extremely hydrophilic after grafting. The interactions between copolymers-coated surfaces, measured using Surface Force Apparatus, as a function of different grafting densities and under different environmental conditions such as ionic strength and pH will be presented.

P16

Water in Contact with Hydrophobic Surfaces: Neutron Reflectometry Studies

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Unravelling the interfacial structure of water at hydrophobic surfaces embodies potential answers to the experimentally observed finite-ranged attractive forces between hydrophobic surfaces in water and the reduced drag on water flowing in hydrophobic channels. These ‘hydrophobic interactions’ are involved in diverse phenomena including protein folding, amphiphile self-assembly, membrane fusion and ‘super-hydrophobicity’. The range and origin of this interaction has remained unresolved for 20 yrs. Here, direct non-invasive neutron reflectivity measurements reveal the presence of a reduced (deuterated) water density region, with a sigmoidal density profile at the hydrophobic silane-water interface that depends on the type and concentration of dissolved gases in the water. Removal of dissolved gases decreases the width of the reduced water density region, and their reintroduction leads to its increase. When compared with recent computer simulations a locally fluctuating density profile is proposed, while pre-existing nano-bubbles are excluded. The presence of a fluctuating reduced water density region between two hydrophobic surfaces and the attractive ‘depletion force’ it leads to, may explain the hydrophobic force, its reported diminution in deaerated water, and the near slip boundary condition for water flowing in hydrophobic channels.

P17

Phase Transition Behavior, Morphological Changes, and Lipid Interactions in Myelin Sheath

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Myelin is a stacked membrane structure that allows for fast, efficient conduction of nerve impulses. It has 8 kinds of lipid molecules on two alternating bilayers and proteins such as Myelin Basic Protein (MBP) which has an important role in maintaining myelin structure. The compact bilayer organization of healthy myelin is believed to require a well-defined range of lipid and protein composition, and bilayer-bilayer interaction. Even though we know that multiple sclerosis (MS) is a morphological transformation involving loss of adhesion between myelin lamellae and sometimes formation of myelin vesicle, its mechanism and causes for demyelination is still under investigation. We have used fluorescence microscopy, Langmuir isotherm, and Langmuir-Blodgett techniques to investigate how lipid composition of myelin lipid system affects the phase transition behaviors of myelin monolayers and bilayers depending on lateral pressure, temperature, and pH conditions. We currently study the topographic changes and the interactions of two symmetrical myelin bilayers in the absence and presence of MBP isoforms using Atomic Force Microscopy (AFM), and Surface Force Apparatus (SFA) techniques. The acute experimental allergic encephalomyelitis (EAE) in the common marmoset which is a highly relevant model of MS was used as a comparison.

P18

Ionization and Molecular Recognition Phenomena in Self-Assembled Surfaces of Bowl-Shaped Macrocyclic Molecules

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The goal of this project is to understand the ionization of self-assembled surfaces of macrocyclic molecules. These molecules act as hosts for recognition of charged guest species. Specifically, self-assembled monolayers (SAMs) of tetrathiol and tetrasulfide derivatives of calix[4]resorcinarene on gold substrates were prepared. Ionization of these SAMs was investigated using a surface plasmon resonance (SPR) technique and contact angle measurements. Solutions of varying pH were used as a probe to test the differences in the advancing angles on these SAMs. As the pH of the solution increases and the surfaces undergo ionization, the change in the balance of interfacial energies is reflected in the contact angle measurements. SPR characterization allows measurement of the optical thickness of ultra-thin films and to monitor the dielectric changes at a solid-liquid interface in a non-invasive and real-time manner. For surfaces of both resorcinarene derivatives, contact angles decrease as the pH of the probe liquid an increases and SPR measurements show that dielectric changes in the surface occur with increase in alkalinity. The results of SPR measurements, contact angle changes and a model for fitting the optical data from SPR will be presented to provide a fundamental understanding of the ionization in the self-assembled surfaces.

P19

Micropatterning of Proteins: a New Approach Using Dewetting Principles

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The ability to control protein and cell positioning on a microscopic scale is crucial in many biomedical and bioengineering applications, such as tissue engineering and development of biosensors. We propose here a novel micro-patterning technique that does not require templates, molds or stencils and is based on patterning polymer films bilayers by dewetting processes, followed by the selective adsorption of proteins from buffer solutions. Evidence is obtained by fluorescence microscopy and atomic force microscopy (AFM) that proteins adsorb preferentially on isolated bio-adhesive micro-patches in a protein-resistant background. The surface density of proteins inside the adhesive islands can be tailored by varying the concentration of the protein solutions employed. Furthermore, the method can also easily produce inverse patterns, containing non-fouling islands in a protein-adhesive matrix. The produced micropatterned substrates should prove useful to studies in biosensor and bioassay development and as substrates to study growth and motility in cell cultures.

P20

Peptide-Modified Responsive Surfaces with Built-in Logic

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The overall thrust of our research program is to develop well-behaved responsive surfaces without the need for complex circuitry or bulky instrumentation. Our approach is to use surface-attached, cross-linked polymer films that can be toggled from a collapsed to a swollen state or vice-versa in response to an external stimulus, which could be temperature, pH, or a small analyte. The stimulus alters the balance of hydration forces in the responsive layer, resulting in changes to the swelling of the layer. We aim to build logic directly into the layer structure via embedded peptides that can modify the balance between hydrophobic/hydrophilic interactions depending on the conformation of the peptide.

Poly-N-isopropylacrylamide (Poly-NIPAAm) is a well-known and studied thermoresponsive polymer. We demonstrate that the transition temperature of poly-NIPAAm networks can be precisely controlled with small peptide sequences. Starting with a poly-NIPAAm network copolymerized with a lysine like monomer, N-(3-aminopropyl)methacrylamide hydrochloride, we show that we can synthesize peptides directly into the Poly-NIPAAm network using standard Merrifield Solid Phase Peptide Synthesis techniques. Ultimately, this strategy will allow ability to formulate peptide embedded Poly-NIPAAM networks with programmable response characteristics.

P21

Long-Range Attraction between Charge-Mosaic Surfaces

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Surfaces with heterogeneous charge density are ubiquitous in biological systems, and it has recently begun to become clear that this non-uniformity of surface charge is crucial in determining their function. In this work we present experimental measurements of the interactions between model surfaces decorated with a mosaic of positive and negative charge patches. The nature of the surface is revealed by AFM and contact angle studies, and the interactions between them, across pure water and aqueous salt solutions, are measured using a Surface Force Balance [1]. We reveal a long ranged attraction between the charge-patched surfaces, and relate these findings to theoretical predictions and models [2, 3]. It appears that the length scale of the interaction is determined by either the patch size or the Debye length, whichever is the shorter.

1. Perkin, S., N. Kampf, and J. Klein, Long-range attraction between charge-mosaic surfaces across water. Physical Review Letters, 96 (2006), 038301.
2. Miklavic, S.J., et al., Double layer forces between heterogenous charged surfaces. Journal of Physical Chemistry, 1994. 98: p. 9022-9032.
3. Evans, D.F. and H. Wennerstrom, The Colloidal Domain. 2nd ed. 1999, New York: Wiley.

P22

Molecular Transport Facilitated Using Corona Charge as a Novel Non-Contact Means

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We have shown here for the first time that application of Corona charge produced in air, to B16 murine melanoma cells in-vitro results in molecular delivery across the cell membrane. Among the many methods of corona discharge one of the methods to generate corona ions is by breaking down of air at room temperature, by the application of a high voltage. The interaction of these charged particles with biological cells was studied and their possible use for molecular delivery was investigated. There is no known work in the literature at this time using this kind of non-contact technique for molecular delivery. Molecular delivery was tested with SYTOX-green nucleic acid stain that is not permeable to cells with intact cell membranes. It was found that there was a significant increase in the amount of SYTOX ($P = 0.003$; statistical significance is assumed for $P \leq 0.05$) delivered to the cells exposed with the corona charge. The results of this study demonstrate that corona discharge can be safely used as a novel means of non-contact molecular delivery. The use of this method will be explored for delivery of drugs and genes to cells in-vitro and animals in the near future.

P23

Society of Women Engineers

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As a member of the chemical engineering community, I have a keen interest in the international thoughts and knowledge in the world of surface materials and their interactions. Through my cooperative education employment with Mosaic Company, the world's largest fertilizer company, I have been introduced to the importance of surface interaction in the manufacturing field. Too many times the interactions on the smallest level are forgotten when looking at such a large picture. Yet, when it comes to chemical reactions, if we do not take into account those interactions, we are remiss in thinking that we understand the fundamental basics of our model. I personally have a responsibility as a student at the peak of my education to seek out resources such as the SFA Conference 2006 to increase my knowledge in my future field.

As President of the University of South Florida section of Society of Women Engineers, I also have an overwhelming responsibility to become more involved in the field of engineering, especially when interacting in the international community. Bringing together world renowned minds is also bringing together a room of persons who can touch the world and our children, helping each young person to possibly decide in a future in engineering. Society of Women Engineers promotes not only getting those young children the information they need to become engineers, but encouraging the women in the engineering world to become more educationally involved in their fields. It is only through international understanding of the lack of female interactions in the engineering field that we will one day have a more balanced field that couples the strengths of both genders.

My hope is that SFA Conference 2006 will offer me the opportunity to learn with the international community. After all, it is only through knowledge that we will ever make a difference.

P24

A Model with Microstates for Rheological Modelling of Complex Fluids

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In this model, the dynamics of a transient network are analyzed by two coupled kinetic processes wich describ the rheological behavior of complex fluids. Five microstates are defined, representing the complexity of interactions among the macromolecules suspended in a Newtonian fluid. These microstates represent statistical networks with varying entanglement density, such as a dense entangled network in one extreme, and free chains or dangling ends (pendant chains) on the other extreme. It is assumed that the energy barrier required to modify the complexity of the system can be provided by the flow, and that the flow-induced change in the network complexity is modeled as a coupled kinetic scheme constituted by a set of reversible kinetic equations describing the time evolution of the microstates. The model predicts shear-banding in steady simple shear and time-dependent non-linear rheological phenomena, such as thixotropy.

P25

Viscoelasticity and Surface Forces in Systems with Alkyl Polyglycoside Surfactants

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The adsorption behavior of non-ionic glycoside, sugar surfactants at the air/liquid and solid/liquid interfaces were studied by using surface laser light scattering (SLS), surface forces and thin film pressure balance (TFPB) techniques. The viscoelastic properties (surface elasticity and surface viscosity) of monolayers formed by isomers of octyl glucoside and 2-ethylhexyl glucoside surfactants were quantified at sub-micellar concentrations and it is shown that diffusional relaxation model describes the observed trends in high-frequency, non-intrusive SLS. The interfacial diffusion coefficients that resulted from fitting this diffusional relaxation model to surface elasticity values obtained with SLS reflect the molecular dynamics of the subphase near the interface. The long-range and adhesive forces acting between non-polar surfaces coated with sugar surfactants were also measured with a bimorph surface force apparatus. After consideration of hydrodynamic interactions the results were compared with disjoining pressure versus thickness curves that were obtained with the thin film pressure balance. It was observed that the stability of thin liquid films crucially depends on the surfactant's bulk concentration (c) and thus on the packing density and viscoelasticity of the adsorbed layer. The force barrier preventing removal of the surfactant layer from between two solid-liquid interfaces increases with increasing c, while for foam films it is the stability of the Newton black film that increases with c.

P26

Microemulsions as Drug Delivery System: Propofol Microemulsions for Anesthesia

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Microemulsions are excellent candidates as potential drug delivery systems because of their improved drug solubilization, long shelf-life, and ease of preparation and administration. Depending on the type of drug, all three types of microemulsions (i.e. oil-external, water-external and middle-phase microemulsion) can be used for drug delivery. In the present study, Propofol (2,6-di-isopropyl-phenol) was selected as a test drug to form water external microemulsion.

Propofol is intravenous general anesthetic drug, having several favorable anesthetic characteristics, including rapid emergence from unconsciousness without drowsiness. Propofol is water insoluble and currently used in a macroemulsion form, which has various side effects. In the present study, several oil-in-water microemulsions constituting Propofol (oil), biodegradable non-ionic Pluronic polymers, and ionic fatty acid salts were formulated. Various properties of these microemulsions, like particle size, stability on dilution, and pH etc. were measured as a function of time, which shows that these systems are stable.

Anesthetic studies of these stable microemulsion systems were done using randomized crossover design in rats. Rats randomly received propofol (10 mg/kg/min) either as a microemulsion or conventional macroemulsion (Diprivan®) to determine these endpoints: induction (dose; stunned; loss of lash reflex, righting reflex, withdrawal to toe pinch) and recovery (recovery of lash, righting, withdrawal reflexes). After 14 days, rats were crossed over into the opposite limb of the experiment. All rats experienced anesthesia with successful recovery although significantly greater doses of propofol were required to induce anesthesia with microemulsions irrespective of surfactant concentration or type.

Propofol microemulsions caused general anesthesia in rat similar to that resulting from macroemulsions. The surfactant concentration and type markedly affects the spontaneous destabilization and anesthetic properties of microemulsions, a phenomenon suggesting an approach whereby pharmacodynamic properties can be selectively modified.

P27

Application of Mesogens to New Write-Once Media for Polarization Holograms

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Holographic storage media such as azopolymers, which can record not only intensity-modulated gratings but also polarization-modulated gratings, have been expected for high signal-to noise ratio (SNR) recordings in the digital data storage. Acting as a wave plate, the polarization gratings can be used to isolate a data signal from the output. The polarization-recordable media, however, cannot fix the polarization modulation because they realign by the following irradiation. We investigated the complex of the azopolymer and photocurable liquid crystals as new hologram media. When the polarized light induced the alignment of the azopolymer, the photocurable liquid crystals oriented as well as the azopolymer by the interaction between the mesogens. Then the only photocurable liquid crystals cured to become polymers and fixed their orientation. This liquid crystal polymer could keep the orientation even after the differently polarized irradiation, while the azopolymer changed the orientation. As a result, we have successfully demonstrated that the proposed complex can act as write-once-read-many polarization-recordable media. Additionally, we obtained the sensitivity of the complex 10 times larger than that of the simple rewritable azopolymer. This effect also depends on the interaction between the mesogens. The sensitivity of the complex kept a certain value even after a serial exposure for multiplexing, while those of well-known photopolymers decreased dramatically. This is because the complex contains the azopolymer that can change the orientation by overcoming the mesogen interaction with the irradiation. The volume multiplexing in holographic data storage requires the constant sensitivity. Therefore, the proposed media, which is polarization-recordable, write-once-read-many and high sensitive, is very promising and practical for digital holographic storage.

P28

Adhesion and Friction of Polystyrene Surfaces: Temperature Effects

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Using a Surface Forces Apparatus (SFA) we have studied the adhesion and friction of polystyrene (PS) thin films on mica having various molecular weights from 580 Da (T_g=-45 °C) to 1,300 Da (T_g=+39 °C). The temperature was varied from 23 to 65 °C, thereby spanning the T_g of the polymers, and the film thicknesses of 30–90 nm were much greater than the radii of gyration ($R_g \approx 1$ nm) of these polymers. Particular attention was given to rate- and time-dependent effects on the adhesion and friction forces. At $T>T_g$ the polymers behave like liquids, and at low detachment and shearing rates their adhesion and friction forces are accounted by their surface energy and bulk viscosity, although fingering instabilities and cavitation accompany the detachment. For the higher MW polymers (PS 1240 and PS 1300) at temperatures below or near T_g, the adhesion and friction forces increasingly depend on the density of chain ends at the surfaces. The adhesion hysteresis peaked close to the bulk T_g, but also depended on the load, contact time, and detachment rate. Certain correlations and scaling relations were obtained, such as the adhesion force *versus* separation rate $V_\perp$, which was found to vary as $V_\perp^n$ where $n \approx 0.15\text{-}0.36$ depending on the experimental conditions. We discuss these findings in terms of the bulk and surface molecular properties of interacting polymer surfaces above and below T_g.