

3B-01

How Do Hydrated Ions Act as the Lubricant between Silica Surfaces in Solutions?; A Nanotribology Study in Aqueous Solutions by AFM

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Understanding of nanotribological phenomena has a critical importance for the fast development of existing and emerging technologies, such as chemical mechanical planarization and microelectromechanical systems. Using Lateral Force Microscopy, we have investigated the frictional interaction between a micron-size silica particle and a silica wafer in solutions under the conditions characteristic for these technologies. It was found the friction force was related with two types of mechanisms: one of them was related to the microstructure of the layer of surface adsorbed cations, the kind of cations and water molecules, and the other one to the microscopic properties of the silica surfaces contacting water.

At high electrolyte concentrations, the hydrated cations adsorbed on the surfaces were found to act as efficient boundary lubricants. The smaller in size and more hydrated cations were, the more frictionless and lubricated two surfaces were. With respect to the pH of solutions, no significant change in the frictional force was found between pH 3 and pH 8. But at pH > 9, the friction force is extremely small in the region of low normal loading force, but it increases exponentially in the region of high loading force. It is suggested that the microscopic property of the silica surface was changed at high pH. The detailed mechanism will be discussed in the presentation.

3B-02

Interaction between polymer, surfactant and colloid studied by a novel force measurement technique

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Using a new force measurement approach,¹ we investigate the role of associative polymers on colloidal forces and its implications on long term stability of the emulsions. This experimental tool has been very effective to obtain insight into the very early stages of polymer-surfactant interaction. It has been found that the interaction between polymer, surfactant and colloid can lead to three distinct scenarios, depending on the sequence of adsorption of polymer and surfactant onto the colloidal interface. In the first two cases, where the colloidal interface is adsorbed with or without surfactant molecules, polymer-surfactant complexation occurs in the bulk phase but without being adsorbed at the interface. Under the above condition, the repulsive force between colloidal droplets is not significantly altered by polymer-surfactant complexes. In the third case, where the polymer is pre-adsorbed at the colloidal interface, polymer-surfactant interaction leads to dramatic changes in repulsive forces (10^{-13} - 10^{-11} N) and onset of repulsion (upto 100nm) due to conformational changes of polymers at the interface, enhancing the stability of the colloid considerably.

3B-03

Investigation of the Role of Geometry and Fluid Structure in the Description of Depletion Forces via Scaled Particle Theory-based Integral Equations for Hard Sphere Fluids

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The ability of colloidal particles to self-organize suggests that colloids could generate complex microstructures for use as templates for advanced materials. Precise control of colloidal dispersions, however, rests on our understanding of the forces between colloids and between colloids and surfaces. Depletion forces, which arise solely due to entropic considerations, are a class of forces which play an important role in colloidal aggregation. Depletion forces are typically modeled with excluded volume arguments, although these arguments usually fail to fully capture all entropic effects. To gain further insight into the origin of depletion forces, we examine the fluid structure of hard sphere colloids near surfaces via a newly derived integral equation based on the scaled particle theory of confined hard sphere fluids. Exact solution of the integral equation, along with simulation results, predicts the appearance of a local density enhancement near the colloid-surface interface. These results suggest that the excluded volume argument is not totally adequate for describing depletion forces and instead the geometry of and the fluid structure near the colloid-surface interface must be considered. Overall, the integral equation lends new insights into the nature of depletion forces and highlights the importance of fluid structure in the understanding depletion interactions.

3B-04

Aggregation Modeling using Sinc Methods

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Aggregation and breakage processes are modeled the population balance equation, which accounts for the particles in the system. The population balance is an integro-partial differential equation that is coupled to the mass, heat and momentum balance equations that are simply partial differential equations. The population balance can be written in various forms, e.g. discrete or cumulative number as well as discrete or cumulative mass, with various bases, e.g. particle size or particle volume, as the internal coordinate. The population balance in all of these forms and bases is still an integro-partial differential equation. This paper solves the cumulative mass population balance in Steigles integral form using Sinc collocation, a finite element method, for several problems including deaggregation of fractal aggregates, aggregation of polystyrene latex particles and the combination of aggregation and breakage of NaCl crystals.

3B-05

The Role of Ultrasonic Analysis in Colloid Characterization

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Most colloid particle characterization has been typically carried out in severely diluted systems employing primarily light-scattering methods. In recent years, ultrasonic analysis has been steadily developed into a viable and attractive option. Ultrasonic analysis permits colloid

characterization at native concentrations, without the need for sample dilution. This presentation provides a review, including recent developments, of the various applications of ultrasonic attenuation, sound speed, acoustic impedance and electroacoustic measurements to colloid characterization.

3B-06

Measurement of the Zeta Potential of Planar Solid Surfaces by Means of a Rotating Disk

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A method of measuring the zeta potential of disks is described. Combining the hydrodynamic properties of a rotating disk, the solution of Laplace's equation for the potential, and the electrokinetic boundary condition, an equation relating the zeta potential of the disk to the streaming potential is obtained. Theory predicts the streaming potential is proportional to the rotation rate raised to the 3/2 power. Placing an electrode near the disk surface and a reference electrode at infinity is shown to be the ideal place to make the streaming potential measurement. Experimental measurements of the streaming potential are made on silicon oxide disks in a dilute potassium chloride solution. The experimental results are shown to agree very well with theory. Determination of the zeta potential using streaming current measurements is also possible, but a current collection efficiency must first be determined because not all the current from a disk flows through the auxiliary electronic current path. Experimental results are shown to agree with published data.

3B-07

Structuring of Nanoparticles and Micelles Confined between Surfaces

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The aim of this work is to investigate the structuring of charged spherical particles between two surfaces as a function of bulk particle concentration. The structuring behavior of the particles can be deduced from the force profiles between two surfaces. In this work, we measure the force between a silica particle and a silica plate in aqueous solutions of particles by atomic force microscopy. We use two types of spherical particles: nanoparticles and micelles. The nanoparticles are Ludox silica, and the micelles are composed of sodium dodecylsulfate. In both of the systems, the force profiles are oscillatory and the wavelength of these forces follows the spacing between the particles in the bulk ($(\text{bulk number density})^{-1/3}$), not the effective size of the particles. At high concentrations of nanoparticles (above 10% by volume) in low ionic strength solutions, the wavelengths of the forces are smaller than the bulk spacing. Addition of salt to these solutions brings the wavelengths back to the bulk spacing. We also perform Monte Carlo simulations to compare with our experimental results and to better understand the structuring behavior of the charged spherical particles confined between surfaces.

3B-08

Charge Instability Induced Breakups of Droplets Containing Ionic Solutes and Suspended Nanoparticles

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We have examined the charge stability limits of single evaporating microdroplets containing ionic solutes and nanoparticles. Droplets were suspended in an electrodynamic balance, and a high precision light scattering technique based on optical resonances was used to determine the size and the size change of a droplet at a charge instability induced breakup. The charge level and the charge loss at a breakup were obtained from the dc voltages required to gravitationally balance the droplet prior to and following the breakup. We have examined diethylene glycol (DEG) and triethylene glycol (TEG) droplets containing lithium chloride (LiCl) as well as suspended polystyrene nanoparticles at varying concentrations. While results on pure droplets of DEG and TEG show that breakups due to the charge instability occur at the Rayleigh limit, droplets containing LiCl solute explode at significantly higher charge levels than the Rayleigh limit. Similar results were observed in droplets containing nanoparticles, that is, a droplet can remain stable at a charge density level greater than three times the Rayleigh limit. The results indicate that the charge stability limit depends on the concentration of solute or nanoparticles as well as the size of nanoparticles in the droplet.

3B-09

The use of the QCM-D technique as a versatile transducer technology for Biosensor applications

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Recent years have seen various biosensor concepts taking the step from the lab into industrial applications. The advance of the quartz crystal microbalance with dissipation (QCM-D) monitoring offers increased information content and flexible routes in the surface chemistry design. In addition, the QCM-D technique is based on an electro-mechanical principle, thus offering label-free and real-time measurements on surface reactions occurring on any solid surface (metal, metal oxide, polymer) in highly viscous and non-transparent liquids. As a consequence, the QCM-D technique offers unique information for designing novel surface chemistries for a large variety of applications, ranging from corrosion studies, via unspecific adsorption of polymers and biomolecules, to specific biorecognition studies. By measuring not only changes in frequency, related to adsorbed mass, simultaneous recording the crystal damping (energy dissipation), theoretical models can be used to deduce structural changes within thin adsorbed layers.

Recent progress nicely illustrates the use of the QCM-D technique as a biosensor platform compatible with diverse surface chemistry architectures, including lipid bilayers,[1] thiol and silane based functionalized self assembled monolayers,[2] functionalized PLL-PEGs,[3] PEI-CMC hydrogels[4] etc. In particular, these surface architectures have been used to immobilize specific detector molecules (i.e antibodies, [4] DNA, [1] coagulation factors, [5] lipid vesicles [1]). In this presentation, the wide-ranging possibilities offered by the QCM-D principle will be

reviewed, with particular focus on different means to immobilize probe molecules for specific bio recognition reactions.

3B-10

Quartz Crystal Microbalance Based on Impedance Analysis – Modeling of Interfacial Layer Properties

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The quartz crystal microbalance (QCM) technique with its many variants is rather mature technique nowadays and it is routinely used to provide information about a range of interfacial processes either in gas or liquid environments. It is widely known that in case of rigid films the QCM works very well as an accurate gravimetric instrument. However, the situation changes dramatically when the QCM is used in certain liquid environments or for studies of thick and soft interfacial layers such as polymers. In such cases the overlayer is often not rigidly coupled to the quartz crystal surface and the response of the QCM also depends on the visco-elastic properties of the overlayer.

We present here how the QCM based on impedance analysis can be utilized to give information on the deviations from rigidity of surface-bound films, and how the measured data can be used for modeling the visco-elastic properties and thickness of the overlayers. We have chosen as model systems one Newtonian liquid, one thick polymer layer in air and a layer-by-layer build-up process of polyelectrolytes in liquid. The modeling used is based on a lumped element approximation of the Transmission Line Model.

3B-11

Multi-Layer Adsorption of Sodium Alginate on Quartz Surfaces: A QCM-D Study of Adsorbed Layer Properties

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Understanding the adsorption of alginates onto solid surfaces is of paramount importance in a wide range of industrial and natural processes. A quartz crystal microbalance with dissipation (QCM-D) is used to study the multi-layer adsorption of alginate as a function of the polysaccharide concentration and ionic strength. Monitoring the rate of energy dissipation with the QCM-D provides insights into the viscoelastic properties of the adsorbed layer of the alginate polyelectrolyte along with the associated ions and water molecules. We show that for alginate concentrations of 0.1 and 1 g/L, the frequency, or adsorbed mass, increases with increasing ionic strength. The variation of the dissipation with the frequency suggests a linear relationship between the mass shift and the dissipation of the adsorbed layer. The normalization of the dissipation by the frequency change due to alginate adsorption demonstrates that the viscoelastic properties of the layer vary as a function of the ionic strength and alginate concentration. The results are discussed in terms of the variations in molecular configuration and compressibility of

the adsorbed layer as a consequence of shielding of the polyelectrolyte charges with increasing ionic strength.

3B-12

Surface Interactions of PGMA-DETA Polymeric Adsorbent in Copper Ion Removal

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Adsorption has gained increasing importance in environmental engineering as a purification method to remove various pollutants, such as heavy metal ions. Surface interactions play a crucial role in the effectiveness of the process. In this study, novel polymeric adsorbent was developed from PGMA (poly-glycidyl methacrylate) and were surface-functionalized with diethylenetriamine (DETA). The resultant PGMA-DETA adsorbent was examined for the removal of copper ions from aqueous solutions. Infrared Microspectroscopy (IR-Microscope) was used to study the surface functional groups and chemical changes with copper ion adsorption. X-ray Photoelectron Spectroscopy (XPS) was utilized to reveal the various surface interactions in the adsorption. It was found that the adsorbent was very effective in copper ion adsorption in pH 4 and 5. In addition to the electrostatic interaction, the IR and XPS results show that surface complexation of the nitrogen and possibly the oxygen atoms with copper ions played an important role in the adsorption of copper ions from aqueous solutions.

3B-13

Effects of an Electric Field on Surface Tension of Conducting Liquids

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Understanding the influence of an electric field on interfacial properties of liquids is of importance from both fundamental and practical standpoints. Charged or electrified liquids currently play a key role in various applications, ranging from microfluidic devices to agricultural treatments. Nevertheless, the effects of the electric field on liquid surface properties are not well-understood, mainly due to the lack of reliable tools and methodologies to measure such effects. A novel methodology, called Axisymmetric Drop Shape Analysis for Electric Fields (ADSA-EF), is developed to measure the effect of the electric field on the surface tension of conducting drops. ADSA-EF matches numerically generated drop profiles with the shape of electrified drops observed in an experiment, taking the surface tension as an adjustable parameter. The best match between numerical and experimental profiles corresponds to the true value of surface tension in the electric field. ADSA-EF detected an increase of the order of one percent in the surface tension of conducting liquids, as well as a second-order correlation between liquid surface tension and the applied electric potential. Details of the methodology along with the experimental results will be presented at the conference.

3B-14

Two Hundred Years of Contact Angle Research (1805-2005)

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This paper provides an overview of contact angle research in the past 200 years starting with the pioneering work of Thomas Young at 1805. It discusses the current thinking in contact angle research and points to the future areas of interest from a technological as well as fundamental point of view. The presentation mainly will center around solid-liquid-fluid systems, but it will also touch on liquid-liquid-fluid systems. Various interpretations of contact angles in terms of solid surface energetics, line tension, and adhesion among other issues will be discussed. Topics of current interest such as superhydrophobicity (ultrahydrophobicity) and contact angle hysteresis will be discussed from theoretical as well as experimental perspectives. Finally, merits of various techniques used in measuring or determining contact angles from ordinary solid surfaces to micro- and nano-spheres will be discussed briefly.

3B-15

Determination of Surface Tension of Fluoropolymers from Contact Angles and the Role of Liquid and Polymer Molecular Properties

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Contact angle data for liquids with bulky, inert molecules on smooth, inert polymer surfaces fall on a smooth curve when plotted as a function of liquid surface tension. If one or more of these conditions is not met, deviations of typically $\sim 1-3$ degrees occur. The existence of such deviations introduces an element of uncertainty in the determination of accurate surface tension of solids. This problem is addressed through contact angle measurements with a large number of liquids of different molecular properties on four different fluoropolymers, i.e. Teflon AF 1600, poly(2,2,3,3,4,4,4-heptafluorobutyl methacrylate), poly(octadecene-*alt*-N-(n -(R_f)-butyl)maleimide), and poly(ethene-*alt*-N-(n -(R_f)-butyl)maleimide). It is shown that the deviations are not an artifact of experimental procedures such as film preparation techniques but have physical causes. Several mechanisms are identified as the possible cause for the deviations: vapor adsorption onto the polymer film, an alignment of liquid molecules in the vicinity of the solid surface, and reorientation of the polymer chains upon contact with the test liquids. It is shown that shape, size, chemical composition, and the molecular configuration of liquid molecules as well as of the polymer chains all play a role. In the light of the results obtained, requirements for the determination of accurate surface tension of fluoropolymer films especially with respect to the probe liquids will be presented.

3B-16

A Methodology for Surface Tension Measurement from the Analysis of Liquid Bridges Shapes

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Surface tension is widely measured using ADSA techniques. These techniques are versatile and accurate in many situations. However, ADSA measurements present a lack of accuracy for small

values of the capillary constant, that is, when working with two liquids of similar densities or when gravity is low. In these situations, the drop shape is not sufficiently sensitive to variations of the surface tension, and ADSA can not measure this quantity accurately. In this work the sensitivity of drops and liquid bridges to surface tension has been studied numerically. Results show that liquid bridges are more sensitive with less volume, so they can provide more accurate surface tension measurements when ADSA fails. The main goal of this contribution is to propose a methodology that uses liquid bridges instead of drops to measure the surface tension value. The principle of this methodology is the same as that of ADSA: the surface tension is measured by comparing the theoretical prediction of the liquid bridge shape to the experimental one. This new methodology has been validated by comparing the results with those given by ADSA in situations when ADSA is reliable.

3B-17

Do Polysaccharides Such as Dextran and Their Monomers Really Increase the Surface Tension of Water?

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It has been reported in the literature that polysaccharides and their monomers increase the surface tension of water. The effect was interpreted as a depletion of the solute molecules from the water-air interface. This paper presents accurate measurements of surface tension of different concentrations of dextrose solution as well as its polymer (i.e. dextran). An automated drop shape technique called Axisymmetric Drop Shape Analysis (ADSA) was used for the surface tension determination. The accuracy of the results was evaluated using a shape parameter, P_s , which has been used to quantify the range of the applicability of ADSA. The results of the above study show that dextrose solutions decrease the surface tension of water in contradiction to the results in the literature. Surface tension decreases continuously with increasing concentration. A similar effect was observed for the dextran solutions.

It is well known that electrolyte solutions, e.g. sodium chloride, increase the surface tension of water. To verify that the setup and the methodology are capable of measuring increases in surface tension, a similar experiment was conducted with a sodium chloride solution. The results obtained from ADSA show that the sodium chloride increases the surface tension of water. It is concluded that dextrose and dextran decrease the surface tension of water. Thus, there is no evidence of depletion.

3B-18

The Interfacial Tension of Spherical and Aspherical Colloidal Dispersions

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The adsorption energy of spherical and aspherical particles onto a liquid-fluid interface and the effect of the line tension are investigated. The results show that without line tension, aspherical particles always prefer to lie flat in the plane of the interface. However, line tension plays a significant role in determining the adsorption of an aspherical particle. First, the line tension

creates an energy barrier for the adsorption of particles onto an interface. The planar configuration has a larger energy barrier due to the longer contact line. Therefore, the particles prefer to enter the interface in a homeotropic configuration and then rearrange to a planar configuration or an oblique configuration with a small tilt angle. Second, for prolate particles, an energy maximum occurs at some tilt angles when the line tension is large. Therefore, once the prolate particle is adsorbed on the interface in a homeotropic configuration or with a larger tilt angle, it must conquer an energy barrier to rearrange to a planar configuration. For cylindrical particles, when the line tension is higher, the planar configuration will not be the most energy favorable configuration. The cylindrical particles prefer to stay in the interface with a small tilt angle.

3B-19

Measurement of Line Tension in Liquid-Liquid Systems

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A new methodology is presented for line tension measurement in liquid-liquid systems. Line tension may be an important parameter for the interpretation of the contact angles of small drops and may play a key role in various technologies such as oil-water emulsion in rocks, stability of foams, micro-fluidic circuits, and microbial systems. Although line tension is a well-defined thermodynamic quantity, controversy regarding both the order of magnitude and the sign of this quantity persists.

The methodology is based on a novel procedure of contact angle determination for a lens of one liquid floating on the other liquid. Line tension is highly sensitive to the measured value of this contact angle. Hence a sophisticated technique (Polynomial Fitting for Line Tension) was developed for high accuracy measurement of contact angles. The proposed system is free from contact angle hysteresis and hence of more immediate thermodynamic relevance than similar work with solid/liquid systems.

The design is able to provide relatively stable and reproducible line tension measurements. Preliminary results using a lens of dodecane at an air-water interface suggests an order of magnitude of 10^{-6} J/m with a negative sign for the line tension. Details and implications will be discussed.

3B-20

Critical Evaluation of the Surface Complexation Model for Metal Oxide Aqueous Interface based on Measurements of Surface Potential

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Ionic equilibria at metal oxide aqueous interface is commonly interpreted on the basis of the Surface Complexation Model that takes into account mechanism of specific interfacial reactions, their equilibrium constants, and the structure of electrical interfacial layer. Several variations of the basic model were used for interpretation of

experimental data. The common experimental techniques are acid base titrations of suspension providing surface charge density in the inner plane, counter ion adsorption measurements and electrokinetics. It was found that these experimental data may be successfully interpreted by several different variations of the model so that one needs to introduce a new experimental technique that might help in solving the problem. There were several attempts to measure surface potential at the inner plane by metal electrodes covered by layer of a metal oxide. However, due to the porosity of oxide layer the data were not reliable. Recently, we have constructed an electrode made of monocrystalline hematite enabling the reliable measurements. These data, together with other data obtained by classical methods, enables evaluation of all parameters characterizing the interface and critical test of the assumptions involved in the application of the Surface Complexation Model.

3B-21

Investigating the Aqueous Surface Chemistry of TiO₂ Pigments using ATR-IR Spectroscopy

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TiO₂ is the most widely used white pigment in the paint and ceramic industries due to its opacity and light scattering, which impart high levels of whiteness and brightness. However the end performance of paint films in categories such as opacity, gloss and colour distribution is directly related to the stability achieved in the pigment dispersion. The stability of the pigment dispersion can be improved by the addition of surfactants, which to date have been chosen based largely on information obtained from empirical methods and without any fundamental knowledge of the surface chemistry involved.

Typical TiO₂ pigments are made up of a particle of rutile between 200 and 300 nm in diameter which is then coated with silica followed by alumina. Pseudoboehmite has been used as a model for the surface of TiO₂ pigments and its aqueous surface chemistry has been investigated using attenuated total reflection infrared (ATR-IR) spectroscopy. The identification of a ligand system that will provide more permanent attachment of a surfactant to the pigment surface has been targeted. The talk will outline the aqueous surface chemistry of pseudoboehmite and TiO₂ pigments.

3B-22

Effects of Charge and Size on Condensation of Supersaturated Water/n-Butanol Vapor on Nanoparticles of SiO₂, TiO₂, d-Mannose, and Rhamonose

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The effects of size and charge on the condensation of a supersaturated water/n-butanol vapor on monodisperse nanoparticles of SiO₂, TiO₂, D-Mannose and Rhamonose were investigated in a flow cloud chamber (FCC). The dependence of the critical supersaturation, S_{cr}, on particle size of a diameter 5 to 30 nm as well as on charge and charge polarity are determined experimentally.

A novel electrospray aerosol generator was developed to generate a high concentration of nanoparticles of less than 10 nm by electrospraying precursors or solution followed by the thermally decomposition or drying. For neutral particles, the experimental S_{cr} decreases with increasing particle size at a rate in a reasonable agreement with the predictions of the Fletcher's version of Volmer's theory of heterogeneous nucleation. For charged particles, the nucleation occurs at a S_{cr} lower than that on neutral particles and the charge effect fades away as particle size increases. In addition, a sign preference is detected, e.g., water vapor condenses more readily on negative charge particle, a trend consistent with those observed on ions. However, both effects of charge and charge polarity on S_{cr} are stronger than that predicted by Volmer's theory for ion-induced nucleation.

3B-23

Preparation temperature dependence of size and polydispersity of thiol-coated gold nanoparticles determined by SAXS

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For the present study monolayer protected gold colloids were synthesized by the Schiffrin procedure, with fixed amounts of the reactants but at various temperatures. The main purpose was to investigate the relation between the preparation temperature and the size of the colloids and their corresponding size distribution. To eliminate possible influences on the mixing procedure of the reductant different series of synthesis were prepared. The water solvated reductant was either added slowly over 30 seconds or added at once to obtain fast reaction. It was expected that the colloids become bigger at elevated preparation temperatures. In order to extend the temperature range in which the colloids can be synthesized, three different methods of synthesizing the colloids in the absence of water were carried out. The first of these methods was to directly add the reductant in its pure form to the reaction mixture, at the second attempt another solvent for the reductant was found and the third one was to try to transfer the reductant to the organic phase with a phase transfer catalyst. The presence and the sizes of the colloids can be ideally analyzed using the method of small-angle x-ray scattering (SAXS). A laboratory SAXS system (NanoSTAR SSS) consisting of Goebel Mirrors, three pinhole collimation and a 2 Dimensional single photon detector (Bruker AXS Inc.) was used for these experiments. A clear trend towards bigger colloid sizes at elevated temperatures was obtained.

3B-24

Size control of nanoparticles during precipitation the BNG way

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Size control of nanoparticles I achieved by controlling nucleation during precipitation and crystal growth after nucleation. The number of crystals formed and the amount of crystalline mass formed determine the crystal size. The balanced nucleation and growth (BNG) model quantitatively correlates crystal nucleation to addition rate, time of reactant addition, solubility,

temperature, and presence of growth restrainers. Experimental results of precision crystallizations will be presented for size control of nano-particles.

3B-25

Synthesis of Platinum Multipods: Control of Anisotropic Growth

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Synthesis of nanostructure with well-controlled morphology has been drawn a great attention recently for its application for tailoring the electronic, optical, magnetic and catalytic properties of advanced materials. Here we report a highly effective synthesis of platinum multipods from platinum 2,4- pentanedionate in organic solvents by Polyol process. A trace amount of silver acetylacetonate is used to trigger the nucleation and the anisotropic growth of Pt nanocrystals. Pt nanoparticles in forms of I- and V-shaped bipods, various types of tripods, and planar and three-dimensional (3D) tetrapods have been successfully synthesized by controlling the reaction temperature, precursor concentration and by using Ag(acac). Transition from multipods to spheres of Pt particles is observed and discussed. High resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD), nanoelectron diffraction and energy dispersed X-ray (EDX) are used to characterize the structures of Pt multipod nanocrystals. A model of formation based on the induced kinetically controlled growth will be discussed.

3B-26

Transport in polymer gels with charged spherical inclusions

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Transport of ions in fluid-saturated polymer gels (e.g., polyacrylamide) with immobile charged inclusions (e.g., silica or latex micro-spheres) is examined under conditions where perturbations to a uniform equilibrium state are driven by (weak) macroscopic gradients of electrostatic potential, pressure or electrolyte concentration.

Electro-migrative, diffusive and convective contributions to the ion fluxes are provided for a wide range of electrolyte concentrations, (inclusion) zeta potentials and (polymer) hydrodynamic permeabilities. The theory, which is not limited by the diffuse double-layer thickness or zeta potential, provides a first step toward a quantitative interpretation of experiments. With the application of an electric field, for example, the particle contribution to the bulk electrical conductivity is obtained. Also of interest, for its influence on micro-mixing and enhanced transport, is the strength of the electric-field-induced flow.

3B-27

Study of Surface Tension of Lung Surfactant: Influence of Humidity on the Properties of the Surface Film

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The surface tension of a lung surfactant, i.e. BLES (Bovine Lipid Extract Surfactant), is investigated using a constrained sessile drop methodology. Preliminary work revealed some irregularities, e.g. certain instabilities of the surface film upon compression. It is shown that moisture plays an important role. At low concentrations of BLES solution (0.5 mg/ml) and in the presence of humidity, the surface films are unstable regardless of the extent of compression, i.e. 5%, 10%, 20%, or 30%. This means that when the film is kept compressed at a surface tension lower than the equilibrium value of ~ 24 (mJ/m²), it cannot sustain the pressure and the surface tension increases towards equilibrium. However, the film is more stable in a dry atmosphere. Apparently, in dry conditions, dehydration of the surface film increases the liquid-crystalline phase transition temperature of phospholipids that are present in the interface. On the other hand in a humid environment, the film is fully hydrated. Hydration of the film decreases the transition temperature of phospholipids and makes them more fluid. Details and implications will be discussed.

3B-28

Binary Colloidal Alloys at Liquid Interfaces – from Super Lattices to Stoichiometric Clusters

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The behaviour of monodisperse silica particles at oil/water interfaces has been studied by microscope observations. Particles of different sizes and/or hydrophobicity and their mixtures have been spread at the liquid interface to give one- or two-component particle monolayers. Strong long range repulsion through the oil between very hydrophobic particles in one-component monolayers has been observed. The particles in these monolayers have been well ordered in triangular lattices at very large interparticle distances (up to ~ 20 particle diameters). In contrast, a weak repulsion between hydrophilic particles has been found. The repulsion is mediated mainly through the water and one-component hydrophilic particle monolayers were disordered and aggregated.

Binary mixtures of large (L) and small (S) very hydrophobic particles have formed two-dimensional super lattices of LS₂ or LS₅/LS₆ type depending on the composition. An interesting selective attraction between very hydrophobic and hydrophilic particles with the same or different sizes has been observed in their mixed monolayers. This resulted in formation of mixed clusters containing one hydrophobic and several hydrophilic particles whose stoichiometry depends on the composition of the mixture. The possible reasons for the selective attraction between very hydrophobic and hydrophilic particles observed at the oil/water interface are discussed.

3B-29

Enhancement of Adhesion to Heterogeneously Patterned Substrates

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Organofunctional silanes have long been used as promoters of adhesion between polymers and mineral oxide surfaces. The present work reports adhesion results obtained using binary combinations of adhesion-promoting and non-adhesion promoting silanes patterned onto an oxide adherend surface. The effects of pattern shape, texture (feature size) and the fractional coverage of the adhesion-promoter are explored for the bonding of poly(vinyl butyral) (PVB) to aluminum (oxide) surfaces using combinations of γ -aminopropyl triethoxysilane (APS), an adhesion promoter, and octadecyl trichlorosilane (ODTS), a non-adhesion promoter for this system. Climbing drum peel tests reveal that adhesion depends on feature size, shape and area ratio of the silanes, in many cases resulting in a reduction of adhesion compared with that for a pure APS film, but in other cases producing enhancements of as much as 80%. Among the conditions examined thus far, the greatest adhesion was achieved using square islands, 12 x 12 mm in size, surrounded by 1.5-mm wide borders of non-adhesive. Adhesion enhancement is attributed to arrest and confinement of crack propagation. As the crack propagates through a heterogeneous surface it will blunt at the end of an adhesive patch, and must re-nucleate at the start of the next adhesive domain.

3B-30

Characterization of Dry Adhesion Between Carboxymethyl Cellulose and Glassine Paper

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A T-peel technique was developed in this study for characterizing dry adhesion between polymer and paper. Several carboxymethyl celluloses (CMC) samples and glassine paper were examined. It was found that this delamination technique was simple, fast, reliable, repeatable, and cost-effective. The modes of interfacial failure and paper failure were observed depending on CMC characteristics and dosage. T-peel force was not affected by the change in peel rate within the range studied. However, the glassine paper showed significant two-sidedness in adhesion to CMC. The results clearly indicated that the adhesion increased with molecular weight of CMC but decreased with degree of substitution of CMC.

3B-31

A molecular dynamics study of the role of conventional and silicon surfactants in the wetting of hydrophobic substrates by aqueous solutions

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Many industrial processes rely on conventional surfactants to increase the wetting of hydrophobic substrates by aqueous solutions. For instance, organic surfactants are added to herbicide solutions in order to achieve a larger wetted area when the solution is applied to the leaf of a plant, which due to the epicuticular wax is a difficult-to-wet surface. For over three decades it has been known that trisiloxane alkoxyolate surfactants or superspreaders are far more effective than conventional surfactants. However, superspreaders are photosensitive, toxic, and relatively expensive. Classical molecular dynamics simulations are being conducted to determine the mechanism by which organic and silicon surfactants increase the spreading of aqueous

droplets on hydrophobic surfaces. Sessile water drops containing either low-molecular-weight alcohols or polyoxyethylene surfactant molecules have been simulated at 298 K on an atomistic graphite lattice. During the course of the simulation surfactant molecules tend to the three-phase contact line where the headgroups are found to interact strongly with water and the tailgroups are directed radially outward and displaced from the droplet. An implementation of the fast multipole algorithm is used for the rapid evaluation of long-range electrostatic forces. Complementary sessile drop wetting experiments are being conducted by our research group.

3B-32

Bovine Serum Albumin (BSA) as an adhesive for wet cellulose

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Bovine Serum Albumin (BSA) was investigated as an adhesive for wet cellulose by 90° peeling of regenerated cellulose membranes laminated with BSA as the adhesive. Drying and curing at elevated temperature (120°C) was required for strong adhesion. Ionic strength of the re-wetting water almost had no effect on wet adhesion. Oxidization of the cellulose membranes to introduce more carboxyl groups onto their surfaces increased the wet peel strength by 60%. Implying the peel failures happened at the protein/cellulose interface. The re-wetting pH of the laminated specimens prepared with oxidized membranes determined the ultimate peel strength while the initial pH of the BSA solution had little effect. The pH dependent wet strength might be good for the pulp recycling.

3B-33

Lattice Boltzmann simulations of drop migration on surface with wettability gradient

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This talk will present results for drop migration on solid surfaces with wettability gradient and chemical roughness. The simulation results were obtained with the Oxford formulation of the lattice Boltzmann method. This formulation has the advantage that one may independently specify physical properties such as the interfacial tension and the viscosities of the phases. Unlike alternative methods such as the boundary element method and the front-tracking method, it is not necessary to track the interface or the contact line. Solid-liquid-liquid systems were used in the analysis. We have found that drops migrate on a solid surface from the hydrophobic side to the hydrophilic side. This appears to be consistent with published experimental studies. Simulations also take into account the chemical roughness of the solid surface. It was found that drops migrate more slowly on a rough surface, which is also consistent with experimental studies.

3B-34

Adhesion between Precipitated Calcium Carbonate and Cellulose Fibre

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The adhesion between Precipitated Calcium Carbonate (PCC) particles and Softwood Bleached Kraft (SBK) Pulp fibres was investigated with a 90 degree peel test of two-ply laminated handsheets. A sparse layer of PCC particles was laid at ply/ply interface and the delamination force was found exponentially reduced with the PCC content as a result of stronger fibre-fibre bonds readily replaced by weak PCC-fibre bonds. The strength of 1.7 μ m scalenohedral PCC-fibre laminates was approximately 1.4N/m compared to 20N/m for filler-free laminates.

Surface coated with carboxymethyl cellulose (CMC) of PCC particles can significantly improve PCC-fibre laminates strength (2.7N/m). However, polyvinylamine (PVAm) can only promote fibre-fibre laminates strength (38N/m) but has no notable effect on PCC-fibre laminates strength. Phosphate containing copolymers with polyacrylamide (PAMVP) and polyvinyl alcohol (PVAP) can also strengthen PCC-fibre bonds with the fact that PVAP is more effective than PAMVP.