

3A-01

Brownian motion in the presence of temperature gradients: An extension of Einstein's theory on the 100th anniversary of its formulation

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Einstein's theory of Brownian motion, which addresses only isothermal fluids, is here extended to situations in which the fluid is subject to an externally-imposed temperature gradient. This extension involves adding a temperature-gradient animated "drift velocity" U to the usual diffusive Brownian contribution appearing in the Fokker-Planck equation governing the particle's conditional probability density. Remarkably, this drift velocity, tending to cause the particle to move towards colder regions of the fluid, is an innate molecular property solely of the solvent in which the Brownian particle is dispersed. Explicitly, U is independent of the Brownian particle's size and shape, as well as of its physicochemical properties. As such, the drift velocity is exactly the same for a macroscopic particle as it is for a molecule of the solvent itself. The underlying theory is supported by experimental thermophoresis data. The ansatz underlying our theory is derived by elementary sedimentation-equilibrium-type arguments of the type invoked by Einstein in his 1905 paper. Here, however, instead of an external force-activated chemical potential gradient causing the Brownian particle's drift, the animation is now caused by the temperature gradient. Consequences of our theory, involving fundamental modifications of the Navier-Stokes and energy equations for nonisothermal fluids, are discussed. (200 words, exactly)

3A-02

Molecular dynamics simulations of nanodrop motion on uniform and non-uniform surfaces

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Results for the motion of nanodrops on solid surfaces will be presented. The results were obtained from molecular dynamics (MD) simulations of drops moving on crystalline solid surfaces. Two driving forces were considered: body forces and wettability gradients. The results indicate that hydrodynamic drag is negligible compared to contact line resistance for drops in the size range considered. A modification of the Blake-Haynes theory was used to model the results of the MD simulations. To obtain values for the Blake-Haynes contact line friction coefficient, MD simulations of drops spreading on uniform surfaces were performed for uniform surfaces having a broad range of wettabilities. In addition, results for the friction coefficient were obtained for receding contact lines. It was found that the friction coefficient for a receding contact line is significantly larger than the friction coefficient for an advancing contact line. The discrepancy between the friction coefficients for advancing and receding contact lines increases rapidly as the surface wettability increases. Since the Blake-Haynes theory makes no distinction between advancing and receding contact lines, a modification of the theory is needed. The modified theory agrees well with the MD results for drop motion on both uniform surfaces and surfaces with wettability gradients.

3A-03

Effects of extreme confinement and field history on the self-assembly of magnetorheological fluid colloids

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The characteristic length scales found in microfluidic devices have been shrinking drastically over the past several years. As a result it is becoming increasingly important to study the effects of this tight confinement. We have used the Brownian Dynamics simulation technique to study the self-assembly of magnetorheological (MR) colloids under confinement. We have examined the effects of extreme confinement (on the order of the size of the MR colloids) and observed that the confinement can induce some very interesting structural properties that deviate from those observed in systems with much less confinement. These deviations manifest themselves in the size of clusters that form as well as the average spacing between the clusters. Additionally we have determined the effects of field history upon the self-assembly of the MR colloids. We have shown that the manner in which the magnetic field is applied can have a significant impact upon the structure as well.

3A-04

Self-Organization of Amphiphilic Copolymers in Aqueous Media

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The assembly of polymers in water is controlled by various extrinsic factors, such as solution temperature, pH, ionic strength and the presence of additives, but it depends primarily on the chemical composition of the polymer and on the sequence of monomer units. Means to direct the assembly of amphiphilic polymers in water will be demonstrated using as examples various copolymers N-isopropylacrylamide (NIPAM). Of particular interest are telechelic PNIPAM samples of narrow polydispersity prepared by controlled free radical polymerization (RAFT). These polymers assemble in various modes depending on solution concentration and temperature. Their properties in water in the dilute regime were examined by microcalorimetry, light scattering, fluorescence spectroscopy and rheological measurements. The properties of telechelic PNIPAMs will be compared to those of sample bearing a few hydrophobes in the middle of the chain, rather than at the chain ends, and to those of telechelic poly(ethylene oxides) of similar sizes.

3A-05

Structure of Microparticles and Nanoparticles in Solid-Stabilized Emulsions

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Emulsions of oil and water stabilized by adsorbed solid particles are known as solid-stabilized emulsions (often referred to as Pickering emulsions). Using confocal microscopy and

environmental transmission electron microscopy, we have studied the self-assembly of colloidal-sized polystyrene particles and alkanethiol-capped silver nanoparticles in Pickering emulsions. Colloidal samples of monodisperse size, when exposed to the emulsion at low concentrations, were found to form small patches with local hexagonal order; these crystalline domains were separated by other particle-free domains. Polystyrene particles with different sizes (1 micron and 4 microns) and different wettability could simultaneously segregate to the emulsion interface and form mixtures on it. In contrast to microparticles, the dodecanethiol-capped silver nanoparticles of 1-5 nm form randomly distributed multilayers at the liquid/liquid interface, with an interparticle distance varying from close contact to approximately 25 nm. Our work offers the first direct observation of nanoparticles in a liquid medium using the environmental transmission electron microscope (E-TEM).

3A-06

Creating Polymeric Nanostructured Networks Through Nucleation and Growth Strategy

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The new season of the material science is beginning. For material scientists, the task of reassembling basic elements now is shifting focus from as-synthesized nanoparticles (first generation) and their single-component assemblies to particles derived from the first-generation ones and supracrystals of different particles. However, nucleation and growth approach, which serves as one of the key strategies to achieve this goal, still remains more like an art than a science. It is the purpose of this study to make a step-forward progress in the quantitative understanding of complex nucleation and growth systems and to use the new knowledge obtained to shed some light on how to use nucleation and growth strategy to fabricate desired nanostructured materials. In this presentation, agarose gelation is used as the typical example. Agarose is a repetitive, essentially uncharged, marine polysaccharide. In the sol state gyration radius of agarose molecules can be as large as ~ 50 nm and behave like typical colloidal particles. In the presentation, kinetics as well as the evolution of the agarose gel topology is elucidated, and the agarose gelation mechanism is identified. It is found that the gelation process can be clearly divided into three stages: induction stage, gelation stage, and pseudo-equilibrium stage. The induction stage of the gelation mechanism is identified using an advanced rheological expansion system (ARES, Rheometric Scientific). It was found that gelation turns out to occur through a nucleation and growth mechanism with a well-defined induction time. The relationship between the induction time and the driving force (supersaturation) follows the 3D nucleation model. A schematic representation of the three stages of the gelation mechanism is given based on *in situ* turbidity and rheological measurements. Further analysis of the kinetics data using 3D nucleation theory indicates that supersaturation driven mismatching between agarose fibrils plays a crucial role in promoting branching, which is extremely important in the network formation. Molecular simulation is employed to support and visualize the proposed interpretation. Based on the knowledge obtained, some comments for building the second-generation nanostructured materials are given.

3A-07

Preparation and Small Angle Neutrons Scattering Characterization of Polysiloxane – silica Nanocomposites

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The incorporation of filler into elastomers imparts many interesting and useful properties to the particle filled composite material. It is well known that the properties mainly depends on the dispersion condition of filler particles and their principal relevant properties : particle size, surface area, filler surface chemistry and on rubber filler interactions.

In the present work, we used Small-Angle Neutron Scattering (SANS) experiments to study the phase transitions in the structure of a composite material made of surface modified silica nanoparticles dispersed in silicone rubber. Self assembling concepts are used in order to explain the role of the silica-rubber and silica-silica interactions on the positioning of silica nanoparticles in three dimensional structures. The phases of interest are the disordered "silica domain" and the long range correlated "fractal silica network".

We investigate again by SANS, whether the fractal network undergoes deformation, reorganization, or breaks at large strains, and correlate the scattering patterns to the mechanical properties of the filled rubber.

From a practical point of view, this presentation is concerned with investigations using model polysiloxane elastomers and silica nanoparticles systems to experimentally elucidate the role of the silica size and surface modification on the long range structure of the silica network.

3A-08

Continuous Polyelectrolyte Nanofilm Growth under an Applied Electric Potential

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Polymer nanofilms offer facile control over the physical, chemical, and biological character of a material surface. Adsorption from solution is a simple means of fabrication, but control over film thickness is limited due to rapid saturation. Thicker, multilayer films are possible, but only through many alternate exposures to solutions of complementary species. We show here that a modest electric potential applied between an adsorbing substrate and a counter-electrode, in the presence of a polyelectrolyte solution, can lead to nanofilm growth that is continuous, without apparent saturation; films of arbitrary and controllable thickness may thereby be realized in a single step. We observe this behavior for poly-L-lysine onto indium tin oxide, at substrate potentials exceeding a threshold (V_{th}), where $0.5 \text{ V} < V_{th} < 0.6 \text{ V}$ (relative to a standard hydrogen electrode), using optical waveguide lightmode spectroscopy (OWLS). Film growth kinetics are initially very rapid and subsequently become linear with time. Linear growth may even be re-established following interruption by placement of a protein layer, suggesting possible applications in biosensing and bioelectronics. Films grown under an applied electric potential exhibit very modest desorption, but are somewhat unstable to removal of the potential.

Chemically cross-linking films using the EDC/NHS method results in greatly improved stability. Atomic force microscopy images reveal films to be particulate, with the particle size slightly exceeding the polymer's hydrodynamic diameter. We find no evidence of electrochemical oxidation at the adsorbing surface, and suspect that secondary structure formation may play a role in the observed behavior.

3A-09

Structure and dynamics of fluorinated fatty acid SAMs by solid-state NMR

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The bonding and chain dynamics of fatty acid monolayers on metal oxides have been previously characterized in detail by solid-state NMR techniques. This current study investigates the structure and molecular dynamics of monolayers of both perfluorinated and semi-fluorinated fatty acids, self-assembled on powdered ZrO₂ surfaces. Self-assembled monolayers (SAMS) have been prepared of perfluorinated fatty acids on ZrO₂ nanoparticles, with chain-lengths ranging from 8 to 18 carbons. The series of semi-fluorinated alkanolic acids F(CF₂)_m(CH₂)_nCOOH, with m = 5, 7, 9 and n = 10, 16, 22 have been synthesized and the monolayers on ZrO₂ prepared. All SAMS have been studied by ¹⁹F-MAS NMR and ¹³C-CPMAS using variable temperature and relaxation techniques. PAS-IR spectra have also been collected for comparison with the NMR data.

3A-10

Dynamic NMR Investigation of Lipid-Hydrotrope Interaction in a Homogeneous System

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It has been reported in our previous study that a homogeneous phase (L1) can be obtained by mixing an appropriate ratio of hydrotrope and lipids. This microemulsion region can be used to prepare unilamellar vesicles by dilution with an aqueous media. It has also been shown that vesicle size is proportional to the lipid/hydrotrope ratio, where the addition of hydrotrope to these systems affects the curvature of the vesicles that form. The nature of lipid/hydrotrope interaction in the L1 phase is important to understanding the vesicle formation mechanism, so as to facilitate the control of the physical and chemical properties of synthesized vesicles

In this study, the L1 phases for lipid/hydrotrope/water systems were systematically investigated using dynamic NMR method. More specifically, NMR T1 relaxation times are measured for the L1 systems made of various hydrotropes with lipid/hydrotrope molar ratios. Among the hydrotropes studied, the discussion will be focused on sodium xylene sulfonate (SXS), sodium cumene sulfonate (SCS), and sodium toluene sulfonate (STS). Due to their structural difference, it is anticipated that the degree of interaction between the hydrotrope and lipid varies. Furthermore, it is hypothesized that subtle differences in lipid-hydrotrope interactions stem from structural variations in the hydrotropes and their ability to solubilize various lipids. This in turn influences physical and chemical properties of the vesicles.

In this talk, some background information on the use of the L1 phase to prepare vesicles will be presented first. The experimental results obtained using dynamic NMR methods including spin-lattice relaxation time measurement will be discussed, especially the correlation between the hydrotrope structure and the lipid-hydrotrope association within the L1 phase. The potential implication of such variance in lipid-hydrotrope interaction on the vesicle formation mechanism will be speculated.

3A-11

NanoLab: a Hands-On Introduction to Nanoscience for Scientists and Engineers

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We have developed a sophomore level laboratory course in nanotechnology. We have taken this hands-on approach to introduce students to the concepts used in nanotechnology much earlier than they would see them in them in the standard curriculum. Although sophomore level students do not generally have the background to understand the full theoretical explanation of all the phenomena, they do take with them a basic understanding that can serve as a framework for appreciating the broader issues when they encounter them in later courses. Topics we have covered are: crystal structure, x-ray diffraction, electron microscopy, electron microprobe, spectrophotometry, extinction, light scattering (Rayleigh & Mie), microfluidics, scanned probe microscopy, and thin-film growth. A report of our experience will be presented.

3A-12

Porous Photopolymer Photonic Bandgap Structures: Fabrication and Applications

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Significant research efforts have been focused on the development of effective means for detecting organic molecules optically using porous one-dimensional photonic bandgap structures. To date, most such work has been based on porous silicon microstructures, which are typically created using a controlled electrochemical etching process in a hydrofluoric acid solution. Generally, these sensors rely on changes in the optical resonance that occurs when the porous structure is occupied by the analyte species, allowing for simple and effective optical detection schemes. Here, we present a simple method for the production of polymeric Bragg reflection gratings containing periodic porous layers, and we demonstrate optical detection of organic solvent vapors using these structures. To create the structures, a pre-polymer syrup containing a monomer, a photoinitiator, a co-initiator, liquid crystals (LC), and non-reactive solvent (acetone or toluene) is sandwiched between two pieces of glass, and the periodic structure is then formed by applying an optical interference pattern generated using a simple one-beam setup. We demonstrate that a few different vapors can penetrate the porous structure and effects a change in the effective refractive index of these gratings, inducing a shift in the reflection wavelength. This shift is pronounced, and can easily be observed by eye, or detected by optical means. We also demonstrate that this shift depends on the vapor concentration, and can be used to reversibly and repeatedly detect the vapor's presence. In addition, we show that

the addition of aminosilane to the pre-polymer syrup improves the stability of the resulting gratings, suggesting that this photopolymer fabrication technique could be used to create structures suitable for biological applications in aqueous environments.

3A-13

Design and Study of Structured Polymer Microspheres

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Multi-layer microspheres may be formed by controlled thermal or chemical imprinting during the particle formation. Specifically, thermal oscillations imposed on precipitation polymerizations of divinylbenzene can be made to produce matching radial density profiles within the microspheres. In this way, onion-type microspheres having up to 20 nested layers may be produced. Similarly, chemical doping of the growing microspheres with suitable comonomers results in distinct layers enriched in functional comonomer. Phenylmaleimide and itaconic anhydride are examples of reactive comonomers that tend towards alternating incorporation and hence form well-defined shells. These comonomers can be used for subsequent shell-specific chemical functionalization of these spheres. The chemical composition of the resulting onion-type microspheres are quantitatively mapped using Scanning Transmission X-ray Microspectroscopy (STXM). Possible applications of these structured polymer microspheres with controlled porosity and functionality as building blocks for 3D photonic band gap devices, and catalyst supports will be discussed.

3A-14

Aggregation in thermosensitive copolymers and related applications

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Some water-soluble natural and synthetic polymers can form hydrophobic aggregates and phase-separate when the temperature is raised. This change can occur at a sharp temperature, known as the lower critical solution temperature (LCST), or over a range of temperatures, depending on their chemical structures and composition. We have found that thermosensitive polymers incorporating natural amphiphilic compounds such as bile acids can even manifest a two-stage aggregation behavior. This can be very useful because of its rheological and technological implications and potential biomedical and industrial applications. We have made several series of copolymers with comonomers such as *N*-substituted acrylamides, bile acid derivatives and even styrene. We found that a small amount of styrene can lower significantly the LCST of the copolymers. A stable emulsion can be formed for such polymers, and they are useful as reversible flocculants and dispersants. The aggregation of the acrylamide copolymers can be facilitated by the presence of the bile acid residues, which can also form micelles with added surfactants. Thermosensitive copolymers are also used as solid support and scavengers in organic synthesis, making the separation process easier.

3A-15

One-pot Synthesis of Block Copolymer Coated Cobalt Nanocrystals

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Reported in this paper is the preparation of ϵ -Co nanocrystals coated by a monolayer of poly(acrylic acid)-*block*-polystyrene or PAA-PS. This method, characterized by its convenience and potential to yield particles with narrow size distributions, is adopted from one using oleic acid as the surfactant. The replacement of oleic acid by PAA-PS as the surfactant during Co nanoparticle preparation yields Co/PAA-PS particles that can be solvent-cast to yield mechanically robust bulk films or 2-d ordered Co particle arrays. For the multi-dentate nature of the PAA binding block, the PAA-PS coating is resistant towards solvent rinsing. The thickness of the coating can be increased by increasing the length of the PS block. Such Co nanoparticles may have many potential applications.

3-16

Passivating Quantum Dots using Polymers

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The molecules at the surface of a semiconductor nanocrystal must fulfil a dual role. In addition to passivating the surface, they must provide an interface compatible with processing and integration steps in manufacturing. For example, water-soluble surface ligands are needed for biological labeling; an electrically conductive layer would be ideal for solar cells; and a polymerizable surface is needed to make photoluminescent polymer composites. A current strategy for meeting these objectives is to replace the ligands introduced during quantum dot synthesis with new ligands, i.e., ligand exchange. We will describe a new approach: use of a multidentate polymer ligand, such as polydimethylaminoethylmethacrylate (PDMAEMA), to modify the surface of CdSe and CdSe/ZnS core-shell colloidal quantum dots. We have found that adsorption of PDMAEMA is accompanied by release of troctylphosphine oxide surface ligands, the process is free of agglomeration, and the modified nanocrystals become soluble in methanol. The photoluminescence properties are well preserved in either toluene or methanol. The polymeric ligands have the following advantages: (a) As-prepared QDs can lose colloidal stability via loss of small molecule ligands that provide only a single binding group (monodentate ligands) to the particle surface. Polymers with many binding groups (multidentate ligands) such as PDMAEMA are significantly more stable to dissociation. (b) The polymer replaces a surface-bound monodentate ligand in dilute solution with high efficacy. (c) The polymer can be functionalized so as to modify the colloidal properties of the QDs

3A-17

New approach to reflective type electrochromic display and the effect of particle size on the color efficiency and switching time

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Reflective type electrochromic display (R-ECD) based on the viologen-modified polymeric microspheres was proposed, and the influence of particle size on the electro-optical characteristics was investigated. At first, the functionalized polymeric microspheres were produced through the seeded polymerization, and then viologen moieties were refluxed on the surface in toluene. In order to control the diameter of viologen-modified polymeric microspheres, the size of polystyrene seed particles was altered using the solvency of medium during the dispersion polymerization. It was confirmed that the color efficiency and switching time of R-ECD were depended largely on the size of polymeric microspheres due to their specific surface area. The particle size and morphology were monitored utilizing an optical microscope (OM), and a scanning electron microscope (SEM), respectively. Redox reactions of the R-ECD were examined by cyclic voltammetry. Reflectance of the R-ECD cell was observed by a spectrophotometer. Response times were recorded using a white LED array spectrophotometer in combination with a digital multimeter.

3A-18

Molecular stars with a three-fold or a six-fold rotation symmetry: Self-assembly and Luminescence

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Two classes of molecule star molecules have been synthesized and investigated by our group. The first class has an approximate C_3 symmetry with three substituent groups attached to either a benzene, a triazine, or a three-coordinate boron central core. The second class has an approximate C_6 symmetry with six substituent groups attached to a central benzene core. The substituent group in both classes is functionalized by either 2,2'-dipyridylamino, 7-azaindolyl, or 2-(2'-pyridyl)benzimidazolyl, which allows further functionalization of the star molecules by metal ions. These two classes of molecules display diverse structures in solution and the solid state. Nanowires formed by self-assembly of some of the 6-fold star molecules have been observed on a graphite surface. The luminescent properties of these molecules are highly dependent on the nature of the functional group and the metal ions present. Some of these molecules have been found to be useful as luminescent sensors for a certain organic analytes. The details of syntheses, structures, luminescent properties of the star molecules and their applications will be presented.

3A-19

Routes of Molecular Energy Transfer over Self-Assembled Surfactant Interfaces

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The intermolecular contacts by which molecular energy is transported across a surfactant interface are observed via IR-Raman spectroscopy. In this technique, an IR light pulse is used to initiate a specific molecular vibration near the interface, e.g. the O-H stretch of a water molecule in a reverse micelle. Following this nascent excitation, time delayed anti-Stokes Raman spectroscopy is used to follow the transfer of the vibrational energy across the surfactant

interface as it is passed from water to the surfactant polar group, to the tail region, and lastly to the nonpolar fluid. Data is presented on CCl₄/AOT/H₂O reverse micelles following independent excitation of water O-H stretch or surfactant C-H stretch. OH excitation reveals energy relaxation of multiple water structures near the interface. Subsequent OH relaxation is strongly coupled to sulfonate vibrational modes of the surfactant head group. The relaxation continues with the sequential movement of energy through the surfactant tail and then into the nonpolar phase. Following CH excitation energy is quickly redistributed among the surfactant head and tail vibrations before it is eventually transferred to the nonpolar phase.

3A-20

Microwave synthesis and applications of semiconductor, metallic and magnetic nanoparticles

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For numerous reasons, there is a growing interest in using alternative and scalable approaches for the synthesis of nanoparticles. Among these approaches, microwave synthesis has received a growing interest lately. Microwave synthesis has been shown not only to enhance the rate of chemical reactions, but also to give better yields in some cases. Our group has recently applied this approach to prepare semiconductor, metallic and magnetic nanoparticles for specific applications [1-3]. Two specific cases will be discussed. First we will discuss the synthesis and characterisation of alloyed Pt-Ru nanoparticles. The integration of these nanoparticles in a polymeric matrix and their catalytical properties for DMFC (Direct Methanol Fuel Cell) applications will be also presented. In the second case, semiconductor nanoparticle preparation and characterisation will be shown. Their utilization for photovoltaic applications will be also discussed.

3A-21

Direct Laser Micro-Patterning of Self Assembled Monolayers

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The ability to engineer surface properties (e.g. wettability, adhesion) at microscopic scale is the key to the emerging technologically important areas such as biosensors, tissue engineering, MEMS, and controlled delivery of liquids in microfluidics. A "Direct Laser Patterning" (DLP) methodology has been developed to manipulate surface wetting properties using a chemisorbed self assembled monolayer (SAM) on gold film (alkenethiol type). This talk will provide an overview of the DLP methodology. It will also report on kinetics of SAM desorption using curve fitting of experimentally measured SAM coverage data at different temperatures to Eyring equation. Activation energy of SAM desorption is calculated to be 30 kcal/mol in air. This information is used in a recently developed thermokinetics model, which describes laser induced

desorption of SAMs through combining SAM desorption kinetics equation with heat propagation equations in DLP methodology. It was found that contrast plots of experimental scanning electron microscopy (SEM) images, which is correlated to surface coverage of SAMs desorbed after laser irradiation, agreed with the theoretically predicted surface composition of SAMs. The surface composition of SAM was then interpreted in terms of the wetting property of the resulting surface. The effect of incident laser beam power and size on final spatial coverage of SAMs on the surface and feature sizes was investigated both experimentally and by modeling. Considering the correlation of the theoretical and experimental results we concluded that the feature sizes are controllable in a predictable way (using the presented thermal-kinetics model) through varying laser beam power and beam size.

3A-22

Preparation of refined Gold nanorods : synthesis, shape separation and optical properties

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Nanoparticle synthesis is characterized by a polydispersity in the shape and size of particles. Since the shape and size determine the properties and applications of nanoparticles, the synthesis of uniformly shaped particles and the separation of desired shape and size from a mixture of different shapes and sizes are necessary. We describe improved seed mediated synthesis of gold nanorods producing a high yield of nanorods with low polydispersity. By understanding the hydrodynamics of nanorods and nanospheres undergoing centrifugation, the efficient separation of gold nanorods from mixture of shapes was achieved. The optical properties of resulting refined gold nanorods are compared to predictions of existing theories, and the main parameters affecting them such as particle size and shape or the dielectric properties of the environment are discussed.

3A-23

Motion of liquid drops on a horizontal surface with a wettability gradient

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Results from experiments performed on the motion of drops of tetraethylene glycol in a wettability gradient present on a silicon surface are reported and compared with predictions from a theoretical model. The gradient in wettability was formed by exposing strips cut from a silicon wafer to the vapors from an alkylchlorosilane. Video images of the drops captured during the experiments were subsequently analyzed for drop size and velocity as functions of time and position along the gradient. In separate experiments on the same strips, the static contact angle formed by small drops was measured and used to obtain the local wettability gradient to which a drop is subjected. The Reynolds, capillary, and Bond numbers in the experiments were relatively small. Even though the velocity of a given drop varied with position on the gradient surface, it is shown that a quasi-steady theoretical model that accounts approximately for the hydrodynamic

resistance and the local driving force adequately describes the observed behavior of the velocity of the drops. Also, it is shown that the instantaneous velocity at a given location in the gradient scales linearly with the planform radius of the drop, as predicted by theory.

3A-24

Surface Properties of Contact Lenses

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Hydrogel polymers can be used as biomaterials, and specifically in ocular applications where specific bulk properties are needed for transparency and oxygen permeability. There is difficulty in controlling these complex formulations as to what species move from the gel matrix toward the surface so as to inhibit or enhance surface interactions, such as encountered with a contact lens in a tear film. Specific surface properties are needed for such complex interactions within aqueous pool of mucin, lipids and proteins. These needs depend highly on the patient's and their wear modality. Additionally in silicone hydrogel polymers, a surface must be rendered hydrophilic, without compromising the surface properties necessary for such deposition resistance. One method commonly used is plasma treatment, which can be used to form surfaces from the bulks' surface moieties or from new surfaces formed from new monomeric moieties. This functions clinically to impart comfort, wettability, deposition resistance and/or a lubricous nature. Selection of the plasma gas / monomer and the process conditions are specific to the substrate being modified. Vastly different surface properties can be imparted which can change the surface morphology, deposition uptake and surface chemistry, as detected by atomic force microscopy (AFM), scanning electron microscopy (SEM), gas chromatography – mass spectroscopy (GC/MS) and X-ray photoelectron spectroscopy (XPS). Characterization of the surfaces' elemental composition using XPS can show less pronounced differences, despite significant changes in morphology and deposition uptake, but such subtle differences play a significant role. Hence, surface properties can be controlled and / or enhanced through the surface plasma chemistry controlled by the gas and process conditions, specific to a substrate chemistry, in an attempt to impart these surface property modifications. A general overview background of the technology and examples will be given.

3A-25

Verification of the Langmuir Isotherm for the Adsorption of Proteins to Polymer Surfaces

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The Langmuir isotherm has been the best fit for the adsorption of proteins to polymer surfaces, which assumes 1:1 binding of an active site on both the protein and surface. This has long been debated since proteins are large enough to make multivalent attachments to surfaces, where n:1 binding seems likely. To explain this discrepancy, we estimated the contact area (A_c) for a single protein molecule anchored to the surface of a polymer by comparing the Gibbs free energy change of adsorption ($-? G_{ads}$, kJ/mol) with the work of adsorption (W_{ads} , mJ/m²). $-? G_{ads}$ was calculated as 20–28 kJ/mol, from the equilibrium constant (K) obtained from isotherm data of albumin/hemoglobin adsorption on plain/carboxylated/sulfonated polystyrene submicron

particles. W_{ads} was calculated as 20–70 mJ/m², based on the surface tensions of water, proteins and polymer particles obtained from contact angle data of five solvents on their thin films. Both $-?G_{ads}$ and W_{ads} decreased as the surfaces became more hydrophilic. Dividing $-?G_{ads}$ by W_{ads} provided $A_c = 0.6\text{--}1.4$ nm²/molecule, which is much smaller than the cross-sectional areas of albumin/hemoglobin (28–40 nm²/molecule). This indicates that only a very small portion of the protein surface is in direct contact with the polymer surface.

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Fibronectin / Polyelectrolyte Multilayer Assemblies: Film Formation and Cell Attachment Studies

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Electrostatically driven layer-by-layer (LbL) self-assembly is a simple and robust method for realizing structurally tailored biomaterial coatings, of thickness ca. 10 nanometers, containing biofunctional ligands. We investigate the placement of fibronectin – a matrix protein useful in tissue engineering applications – onto multilayer films formed by the alternate deposition of poly-L-lysine (PLL) and dextran sulfate (DXS). We use optical waveguide lightmode spectroscopy (OWLS) and quartz crystal microbalance with dissipation (QCM-D) to characterize film formation in situ. We find fibronectin adsorption to a film terminated with PLL to exhibit rapid kinetics and a large saturation, and to be essentially irreversible. In contrast, fibronectin adsorption to a film terminated with DXS is characterized by slower kinetics and a more modest saturation, and is partially reversible. We find no evidence of fibronectin penetrating the multilayer film. We use optical microscopy to determine the influence of fibronectin/polyelectrolyte multilayer assemblies on human umbilical endothelial cell (HUVEC) behavior. We observe the addition of fibronectin to DXS terminated assemblies to result in drastically increased HUVEC spreading and circularity. In contrast, the addition of fibronectin to PLL terminated assemblies leads to only subtle changes in the HUVEC response. We discuss this key difference in terms of the structure of the adsorbed fibronectin layer as well as the charge and hydration of the multilayer film.

3A-27

Surface Assembly of Protein in Correlation to Protein Crystallization

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The assembly of lysozyme (hen egg white) at the surface of aqueous solution follows the same behaviors as amphiphilic molecules. The critical assembly concentration appearing in the protein solutions is found to coincide with the equilibrium concentration of protein crystals under given conditions. The crystallization of protein regarded as a typical case of protein self-assembly in three dimensions has been discussed. The result reveals also the correlation between protein crystallization and the two-dimensional self-assembly at the surface of substrates. It follows that the protein crystallization conditions can be determined without protein crystals.

3A-28

Surface Treatment with Polymers for Biofouling Retardation

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Polystyrene (PS), polyethylene (PE), polypropylene (PP), glass, and stainless steel were exposed to aqueous solutions of a series amphiphilic polymers at room temperature, including poly(N-isopropylacrylamide) (PNIPAM), polypropylene oxide (PPO)-polyethylene oxide(PEO) block copolymers and PEO. Dynamic contact angle measurements of the material surfaces before and after the treatment indicated that: (1) almost no adsorption of PEO on PS, PE, and PP surfaces; (2) PPO-PEO copolymers adsorb only minimally on PE and PP surfaces; (3) PNIPAM adsorbs on both hydrophobic and hydrophilic surfaces. The surface morphologies of the materials before and after polymer adsorption were investigated by profilometry. Protein adsorption on PNIPAM pre-adsorbed surfaces was investigated by dual polarisation interferometry (DPI) and profilometry using lysozyme as the model protein. The results obtained indicate that PNIPAM can significantly improve the bio-deposition resistance of artificial surfaces, making PNIPAM treatment attractive for preventing biofouling of protein separation membranes and biomedical devices.

3A-29

Atomic Force Microscopy Studies of Langmuir-Blodgett Films: Storage Protein from Aleurone Cells of Barley and Lipid Associations

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The adsorption of storage globulin protein from aleurone cells of barley (*Hordeum vulgare L*) on lipid films (e.g. dipalmitoyl phosphatidyl choline: DPPC or stearic acid: SA) at the air/water interface was studied by Langmuir-Blodgett technique (LBT) and tapping mode atomic force microscopy (AFM). The behavior of protein is complex generating large colloidal particles which appear to strongly adsorb on the lipid monolayers. The obtained results indicate a long range order within protein, protein:DPPC and protein:SA layers, as well as electrostatic effects, and lipid surface and protein attraction. The protein layer shows a unique structural pattern in its adsorbed state that might laid down during grain development and it can generate complex supramolecular structures involving various classes of biological molecules, e.g., lipids, natural pigments or combination of those. Due to the high stability of protein layers, the storage protein might fulfill the key requirement as building blocks for the production of novel supramolecular materials as required in molecular nanobiotechnology and biomimetics.