

2-01

Nanosize Particles as Building Blocks for Uniform Colloids of Different Morphologies

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This talk will address the problems involved in the formation of uniform colloids of different particle shapes. Specifically, the focus will be on the mechanisms by which such particles are generated by aggregation of nanosized precursors. Both chemical and physical aspects of the involved phenomena will be illustrated.

2-02

Applications of Light Scattering Techniques for Determining Doublet Formation Rate of Colloidal Systems

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The formation rate of a doublet from two primary particles is one of the fundamental characteristics of a colloidal system. It gives direct estimate of the Fuchs stability ratio W , which can be used to estimate the effective surface charge and is also a prerequisite in the simulations of aggregation kinetics using the population balance equations. Among the available techniques in the literature, those based on light scatterings are most commonly used, because they are noninvasive and supported by sound scattering theories. However, those relying on the dynamic light scattering have ignored the effect of the rotational motion on the measured hydrodynamic radius of the doublets. In the present work, we analyze and show that this effect is significant for a doublet, in the cases of $qR_p > 1$ (q is the scattering wavevector and R_p is the radius of primary particles). Thus, before such an effect can be quantified, care must be taken in the applications of the dynamic light scattering to determine the doublet formation rate. Therefore, we have proposed a technique that is based only on the static light scattering (SLS) experiments to determine the doublet formation rate. In particular, this technique monitors the very initial stage of the aggregation, where the system is dominated by only primary particles and doublets. It first determines the conversions of the primary particles to doublets x at different aggregation times by reconstructing the average structure factors of the aggregating system obtained from the SLS experiments. Then, considering the second-order kinetics of the doublet formation, we can obtain the doublet formation rate from the time-dependence of the conversion x , which in turn gives the estimate of the Fuchs stability ratio W . Several aggregation experiments have been carried out to demonstrate the applicability of the proposed technique.

2-03

Destabilization of silica nanoparticles suspensions with Al_3 polycations

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Although Al_3 polycations ($Al_2^{VI}(OH)_{24}Al^{IV}O_4(H_2O)_{12}^{7+}$) are widely used as coagulants in the water treatment industry, the mechanisms by which they interact with colloidal particles suspended in water and induce their aggregation are not fully understood. We study here how silica sols with different particle sizes in the range 10-25 nm and with pH adjusted to 5 or 9 are destabilized with addition of Al_3 polycations. After turbidimetric determination of the aggregation kinetics, the interactions between silica and Al_3 as well as those between nanoparticles in presence of Al_3 are characterized. The aluminum species present both at the surface of particles and in the dispersion medium are identified using ²⁷Al NMR spectroscopy, whereas osmotic pressure measurements allow us to

investigate the modification of interactions between particles with the rate of added coagulant and pH of the dispersion. Small angle neutron scattering experiments provide us additional information about interactions between particles but also about the structure of the aggregates formed. Beside the differences revealed in the aggregation kinetics and the amount of Al_3 required for aggregation at pH 5 and 9, suggesting different destabilization mechanisms, the variation of the aggregation conditions appears as a mean to control the morphology of the silica aggregates.

2-04

Heteroflocculation induced by montmorillonite plates acting as bridging agents

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In papermaking, a microparticulate retention aid system consisting of bentonite and high molecular weight cationic polymer is commonly used to incorporate mineral pigments in the fiber web. It is believed that the mechanism by which bentonite operates is based on the ability of montmorillonite (its main component) to form a bridge between polymer-covered fibers and colloidal particles, resulting in heteroflocculation. Its performance appears to be related to its ability to delaminate montmorillonite. A common way to promote montmorillonite delamination is treating it with sodium-rich solutions. A novel way of enhancing montmorillonite delamination is to break-up aggregates of fibers held together by montmorillonite stacks. The extent of montmorillonite delamination was evaluated by measuring the deposition of calcium carbonate pigments on fibers coated with cationic polyacrylamide suspended in water. The results show that the flocculation efficiency of montmorillonite strongly depends on its ability to delaminate. Montmorillonite is most effective when it is completely delaminated, in which case single plates form strong bridges between polymer-coated particles.

2-04

Controlling porosity within colloidal heteroaggregates

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Heteroaggregates of cationic poly(2-vinylpyridine) microgels, anionic polystyrene latex and anionic silica particles have been made by mixing dilute, aqueous suspensions. The resulting heteroaggregate flocs were then concentrated by vacuum filtration, freeze dried, and characterized by mercury porosimetry, SEM and TEM imaging techniques. Control of the pore volumes within the dried filter cakes is demonstrated by two techniques. In the first technique, heteroaggregation at a constant KCl concentration was stopped or 'arrested' by the subsequent addition of silica particles, thereby limiting the size of the flocs. Pore volume was shown to increase as the aggregation time prior to 'arrest' was increased. In the second technique, the aggregation time prior to arrest was maintained constant while the KCl concentration was varied. The pore volume of the aggregates decreased as the electrolyte concentration increased. The method of arresting the heteroaggregation potentially allows high volume fractions of flocs to be made without the formation of a gel which is difficult to process, thereby providing a method of manufacturing materials with controllable porosity. In addition, incorporation of swellable microgels in a porous structure offers potential for creating novel structures suitable for controlled release applications.

2-06

Aggregation Kinetics of Alginate-Coated Hematite Colloids in Divalent Electrolytes

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Aggregation kinetics of alginate-coated hematite colloids is measured in the presence of divalent electrolytes (CaCl_2 and MgCl_2) by dynamic light scattering. It is shown that alginate undergoes inter-polymer binding in presence of calcium ions, but not with magnesium ions. The aggregation kinetics of the alginate-coated hematite colloids in the presence of the divalent cations is compared with the kinetics in monovalent electrolyte (NaCl). We find that the alginate-coated hematite colloids undergo aggregation by electrostatic destabilization with sodium or magnesium ions, while the aggregate growth rate is much higher with calcium ions. In the case of aggregation with calcium ions, transmission electron microscopy (TEM) reveals hematite colloids enmeshed within clusters of alginate network. We propose that the enhanced aggregation with calcium ions is due to the formation of extended alginate cross-links around the alginate-coated colloids, which greatly increases their collision radii. It is also found that the presence of sodium as a background electrolyte is detrimental to this calcium-induced enhanced aggregation.

2-07

Light driven aggregation of core-shell chromophoric colloids

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A photo-controlled aggregation in non-polar solvents has been achieved using spirobenzopyran methylmethacrylate (SP-MMA) polymer layers grafted from silica particles. The chromophoric molecules incorporated into these core-shell architectures can be switched from a non-polar closed form (spirobenzopyran) to the open, zwitterionic form (merocyanine) through exposure to ultraviolet (UV) irradiation ($\lambda \sim 360$ nm). Subsequent visible light irradiation ($\lambda \sim 540$ nm) or heat treatment reverses this process. Here, this molecular isomerization reaction was employed to drive colloidal aggregation in border-line solvents. The process is reversible, with the requirement of agitation to redisperse the particles following agglomeration. System fatigue is minimal yielding reproducible results even after a large number of cycles. Dependence of sedimentation behavior on solvent polarity and chromophore content within the SP-MMA layers, system rheological response, and particle adsorption behavior onto optically patterned surfaces are discussed.

2-08

Crystalloluminescence in the Synthesis of Nanosized Particles

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A new nucleation theory will be presented which allows the prediction of the particle size distribution of atomic clusters. This theory accounts for the collisions of atoms with clusters and clusters with other clusters according to the free energy driving force for their collision and the frequency of their collision by various mixing methods. The frequency of their collision can be predicted by either diffusion or shear induced or turbulence induced models. The free energy for these collisions is a function of the bonding geometry of the initial cluster(s) and resulting cluster. This free energy information is available in a limited number of alkali metal systems from quantum mechanics. The resulting partial differential integral equations are solved for limiting cases, which are used to predict the cluster size distribution. Another benefit of this theory of nucleation is an explanation of

crystalloluminescence - light produced during nucleation, which can be used to control the nanosynthesis process so that a very narrow range of clusters is produced.

2-09

Fabrication of novel types of colloidosomes and liposomes with gelled cores

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Colloidosomes and liposomes are core-shell structures that consist of an aqueous core and a shell formed by fused colloidal particles or lipid bilayers. Recently, it has been recognised that such microcapsules offer a great potential in controlling the permeability of entrapped species in pharmaceutical, cosmetic and food products.

Here we report a versatile fabrication method of novel colloidosome microcapsules which is based on the following 3 stages: (i) Hot aqueous solution of gelling hydrocolloid is emulsified in a suitable oil in the presence of solid polymer particles dispersed in the aqueous phase to produce a water-in-oil emulsion stabilised by the solid particles and the system is cooled off to set the gel. (ii) The produced suspension of aqueous gel microcapsules coated with a particle monolayer is separated by filtration to remove the oil phase. (iii) The microcapsules are washed and collected into water. This methodology allows us to produce colloidosome microcapsules of diameters varying between several tens of micrometers to several hundreds of micrometers. The function of the gel cores was to support the particle shell around them and to give the microcapsules enough stiffness to be separated from the oil phase by filtration.

Following this technique we have been able produce three different types of colloidosome microcapsules. (a) By combining monodisperse amino-latex microparticles and an oil which swells the latex we have fabricated integral colloidosomes of porous membrane where the pore size is controlled by the degree of swelling. (b) By using monodisperse amino-latex particles and cross-linking agent we were successful in producing colloidosomes of spherical particle monolayers, where the membrane pores are defined by the particle size. (c) By using polymer micro-rod particles as emulsifiers we have synthesized for the first time “hairy” colloidosomes which shells consists of randomly assembled rod-like particles.

We also report the fabrication of novel hybrid giant liposomes with cores of an aqueous gel based on an extension of the Pautot technique. It involves the following three steps: (i) A lipid-stabilised water-in-oil emulsion is prepared in the presence of a gelling hydrocolloid in the aqueous phase. (ii) The water drops, coated with a lipid monolayer are gelled at lower temperature to produce gel beads. (iii) The gelled beads are transferred from the oil phase through the planar oil-water interface where they pick up a second lipid monolayer and convert into giant liposomes of gelled aqueous cores. We maintain a saturated lipid monolayer at the planar oil-water interface by injecting lipid solution in a spreading solvent. These novel microcapsules have higher stability and mechanical strength than conventional liposomes and may find applications as drug delivery vehicles and for controlled release of proteins, vaccines, cosmetic and food supplements.

2-10

Aggregation, cluster formation and gelation in colloidal suspensions: From photonic liquids to equilibrium clusters and gels

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With the equilibrium behavior of colloidal systems seemingly well-understood, attention recently turned to non-equilibrium phenomena. In particular the influence of attractive interactions of variable strength and range has been investigated intensively, and it has been demonstrated that the presence of a short ranged attraction can lead to fascinating phenomena that include metastable liquid-liquid phase separation and dynamically arrested states such as attractive and repulsive glasses as well as transient gels. These issues of interparticle interaction, aggregation, cluster and crystal formation and dynamical arrest are of central importance to a variety of topics ranging from cluster formation in various diseases to the production of photonic crystals.

In my lecture I shall outline the various aggregation phenomena that can be observed upon combining short or long range attraction with either a hard and/or soft repulsion. I shall in particular aim at demonstrating the generality of the emerging description on the phase behaviour of a wide range of colloidal suspensions.

2-11

Direct Imaging of Phase Behavior and Structure of a Strongly Adsorbing Microsphere - Nanoparticle System

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We have investigated the phase behavior and 3D structure of a model microsphere-nanoparticle system possessing high charge and size asymmetry in which polystyrene nanoparticles ($D = 21$ nm) strongly adsorb to silica microspheres ($D = 1.18$ μ m). By varying the nanoparticle:microsphere ratio, we can tailor the transitions between stable fluid and attractive gel phases. Using confocal fluorescence scanning microscopy, we directly observe their 3D structure of as a function of varying composition. In the absence of nanoparticle additions, the electrostatically charged microspheres reside in a stable fluid phase that crystallizes upon sedimentation. As the nanoparticle concentration is initially increased, strong gelation occurs via nanoparticle bridging between colloidal microspheres. At higher nanoparticle concentrations, nanoparticle-coated microspheres are again stabilized by electrostatic interactions. We demonstrate how this fluid-gel-fluid transition can be utilized to control the morphology of both colloidal crystals and gels formed under gravity-driven sedimentation.

2-12

Direct visualization of the coupled aggregation and sedimentation of weakly interacting colloid-polymer mixtures

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Particle aggregation is of great interest not only due to its occurrence in biological systems, paints and coatings, and numerous foods, but also due to its fundamental role as a simple model system for growth under non-equilibrium conditions. In the past decade, most work has focused on the cluster geometry and growth kinetics in the absence of sedimentation. However, many real aggregation phenomena are influenced by sedimentation. The knowledge of colloidal aggregation in a gravitational

field will help to create a thorough understanding of processes occurring in real aggregating systems. Through the use of confocal microscopy, we investigate the coupled aggregation and sedimentation of colloidal particles in polymer solutions as a function of the strength of attraction between particles. We discover that strong coupling between aggregation and sedimentation occurs which limits the growth of clusters depending on the magnitude of attractive forces, resulting in structures of various degrees of compaction. Lastly, we examine the aging of the sediments. Internal restructuring due to gravitational stresses drives the compaction and rearrangement of the gel with time. At high polymer concentration, the particle-particle bonds are not easily broken and the flocs cannot freely reorganize to form compact structures due to the high magnitude of the interaction at contact.

2-13

Aggregation Time Required for the Bottom-Up Assembly of Colloids

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Numerous studies have demonstrated the bottom-up assembly of complex structures such as colloidal crystals, close-packed aggregates, and even rings and tetramers. We show the production of a simple localized and nanoscale charge distribution on the surfaces of individual colloidal microspheres using our technique of “particle lithography”. In this technique, parts of the microspheres are masked off, while polyelectrolytes cover the remaining portions of the microspheres. The effectiveness of this process is demonstrated by the accurate and reproducible production of colloidal heterodoublets composed of oppositely-charged microspheres. The particle lithography technique is advantageous since it is not limited by the resolution of photolithography or by functionalizing chemistries. A key challenge for the processing of heterodoublets and more complex aggregates is knowing the time required for the assembly to occur. A model has been developed that relates the aggregation times of the colloidal microspheres to their size and concentration in the assembly suspension. This model investigates the Brownian rotation of the microspheres and gives predictions about the experimental times required for the particle lithography technique. Results are presented for the formation of heterodoublets and the aggregations times of microspheres with varying particle suspension conditions.

2-14

Film Formation and Gelation Process Studied by Multispeckle DWS

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We present in this work a new optical technique to study film or gel formation from colloidal systems. Our technology is based on diffusing wave spectroscopy (DWS), an extension of classical dynamic light scattering (DLS) to concentrated and opaque media. This new, non-invasive and very simple technique allows monitoring of the “media movement speed” from all kind of dispersed systems such as latexes, emulsions, or solvent-born suspensions. Using a laser source and a video camera as receptor, we have developed an original multi-speckle DWS technique using a simple and direct processing of the light backscattered from the system. The kinetics of bulk aggregation is displayed in real time by specific software.

Different film forming products have been investigated (e.g., water-based, solvent and solvent-free paints, inks, adhesives, varnishes, coatings) on various types of substrates (e.g., metal, plastic, glass, PMMA) and at different thickness from few microns to hundreds of microns. Preliminary experiments on gelation of yoghurt and gelatine have also been performed. From the kinetics, a wide range of information can be extracted such as objective gelation or drying times (e.g., dust-free, touch-dry, dry-

hard), mechanism taking place (e.g., solvent evaporation, coalescence, cross-linking), thereby offering new possibilities to investigate these complex colloidal systems.

2-15

Role of Electrostatic Interactions in Bacterial Deposition

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The influence of bacterial electrokinetic properties and surface bound lipopolysaccharides (LPS) on cell deposition (adhesion) are examined using three mutants of *Escherichia coli* K12 with well-characterized LPS of different lengths and molecular composition. Two experimental techniques, a packed bed column and a radial stagnation point flow system, are employed to investigate bacterial adhesion kinetics onto quartz surfaces over a wide range of solution ionic strengths. Although the two systems capture distinct deposition (adhesion) mechanisms because of their different hydrodynamics, similar deposition kinetics trends are observed for each bacterial strain. Bacterial deposition rates are directly related to the electrostatic double layer interaction between the bacteria and quartz surfaces, in qualitative agreement with classic DLVO theory. However, DLVO theory does not fully explain the deposition behavior for the bacterial strain with the lengthy, uncharged O-antigen portion of the LPS. Neither the length nor the charge characteristics of the LPS molecule directly correlated to deposition kinetics, suggesting a complex combination of cell surface charge heterogeneity and LPS composition controls the bacterial adhesive characteristics. It is further suggested that bacterial deposition behavior is determined by the combined influence of DLVO interactions, LPS-associated chemical interactions, and the hydrodynamics of the deposition system.

2-16

Study of Correlation of Adsorption and Interaction of Ceria Nanoparticles with Silica Surface

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Using light scattering technique, we developed a new method for detection of the adsorption of ~50 nm ceria particles on silica wafers. Adsorption of the particles was studied in aqueous solutions of different acidity, pH 4,5,6,7,8, and 9. It is of fundamental interest to compare these data with the forces between individual particles and silica surfaces. We use the atomic force microscopy (AFM) to measure such forces directly. We report a new method to modify the AFM probe to get a single nanoparticle on the probe apex. Using this method, we are able to study the interaction between individual ceria particles and silica surface, both long-range and contact (adhesion) forces in aqueous solutions of the same acidity as above. The obtained data and correlation between the measured adsorption and forces are discussed.

2-17

Marangoni effect reverses coffee-ring depositions

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We report here that Marangoni effect reverses coffee-ring depositions. Most of particles deposit at the center of the droplet, rather than the edge, due to a Marangoni flow induced during droplet

evaporation. We develop a full analytical solution to the *temperature and velocity fields* in the drying droplet to analyze the particle deposition process. The measurement of the fluid flow in the drying droplet confirms our theoretical analysis. Combining the analytical solution for the flow field with Brownian dynamics simulations, we are able to compare our experimental results for particle deposition with predictions. The good consistent between experiment and theory is obtained.

2-18

Controlled Deposition and Modification of Conductive and Antireflective Nanoparticle Coatings

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The convective assembly method for particle deposition was originally designed for assembling colloidal crystals from monodisperse particles for photonic applications. However, we will demonstrate that the method allows facile controlled fabrication of nanoparticle coatings with a range of other useful properties. Two types of nanocoatings that will be presented are conductive metallic films from gold nanoparticles, and antireflective (AR) films from silica microspheres. Uniform nanocoatings were deposited in minutes directly from aqueous suspensions by convective assembly at high volume fraction. Operational ‘phase’ diagrams were constructed, relating the crystal layer thickness and packing symmetry to the process parameters. The deposition process allows control over the coating thickness, number of layers, optical properties, and the electric conductance of the films (in the case of the gold nanocoatings). By varying the deposition speed of the AR silica coatings, the band of optimal transmission could be tuned across the breadth of the visible spectrum (from 450 to 650 nm). The AR coatings were further optimized by the use of particle mixtures, which reduced the reflectance loss on glass by up to 89%. The nanocoatings developed could be used in applications ranging from nanoelectronics to energy efficient windows and solar cells.

2-19

Faradaic Reactions as the Source of Net Interparticle Motion Driven by ~100 Hz Alternating Electric Fields

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Over the past decade, observations of net interparticle motion above a planar electrode due to alternating electric fields have been explained by multiple different force mechanisms. While past results indicate that multiple mechanisms are dominant over different frequency ranges, at frequencies for which electrode reactions are important, new results suggest that these reactions are the root cause of both net lateral and vertical particle motion. This talk details the connection between the vertical forces induced by the application of an alternating field in the 30 Hz to 250 Hz frequency range, and new predictions of electrolyte dependent lateral motion that closely match published experiments.

2-20

Galvanic Cell Mediated Colloidal Crystallization

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We report a novel method for assembling micropatterned colloidal crystals using *in-situ*, spontaneous, galvanic action whereby crystalline arrays can be created by a “galvanography” technique. For example, by confining particles to shallow trenches, two-dimensional (2D) ordered single crystals were formed. We observed a sort of repulsion of silica particles from oppositely charged galvanic electrodes and crystallization on those with the same polarity. These are counterintuitive based on electrostatic considerations and appear to result from a bulk electroosmotic fluid flow (EOF) associated with galvanic process. To our knowledge, this is the first report of electrokinetics in the

context of the centuries-old galvanic cell concept. This technique has applications in the construction of electrophoretic microchips for the separation of particles with different surface charges. In addition to the activity of a bimetallic galvanic cell, a single polycrystalline metal will also induce preferential colloidal crystallization via galvanic processes.

2-21

In Situ Layer-by-Layer Film Formation Kinetics under an Applied Voltage Measured by Optical Waveguide Lightmode Spectroscopy

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Layer-by-Layer (LbL) thin film assembly occurs via the alternate adsorption of positively and negatively charged macromolecular species. We investigate here the control of LbL film growth through the electric potential of the underlying substrate. We employ optical waveguide lightmode spectroscopy (OWLS) to obtain in situ kinetic measurements of poly(allylamine hydrochloride)/poly(sodium 4- styrenesulfonate) (PAH/PSS) and poly(L-lysine)/dextran sulfate (PLL/DXS) multilayer film formation in the presence of an applied voltage difference (DV) between the adsorbing substrate, an indium tin oxide (ITO) coated waveguiding sensor chip, and a parallel platinum counter electrode. We find initial layer adsorption to be significantly enhanced by an applied potential for both polyelectrolyte systems: the mass and thickness of (positively charged) PAH and PLL layers on ITO are about 60% and 500% larger, respectively, at $DV = 2$ V than at open circuit potential (OCP), in apparent violation of electrostatics. A kinetic analysis reveals the initial attachment rate constant to decrease with voltage, in agreement with electrostatics. To reconcile these results, we propose a more coiled and loosely bound adsorbed polymer conformation at higher applied potential. Following 10 adsorption steps, the mass and thickness of a PAH/PSS film grown under $DV = 2$ V are about 15% less than those of a comparable film grown under OCP, reflecting a lower degree of complexation between adsorbing polyanions and more highly coiled adsorbed polycations. Following 14 adsorption steps, the mass and thickness of a PLL/DXS film grown under $DV = 2$ V are about 70% greater than those of a comparable film grown under OCP, reflecting the increased charge overcompensation in the initial layer. We find the scaling of film mass (M) with the number of adsorption steps (n) to be linear in the PAH/PSS system and exponential in the PLL/DXS system, irrespective of applied voltage. The formation kinetics of PLL/DXS, but not PAH/PSS, change qualitatively under voltage: PLL adsorption is slow to reach a plateau, possibly due to the formation of secondary structure, and a decrease in film mass occurs toward the end of each DXS adsorption step, suggesting a spontaneous removal of some PLL/DXS complexes from the film.

2-22

Secondary Energy Minima and Surface Charge Heterogeneities Cause Breakdown of Classical Filtration Theory

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The mechanisms and causes of deviation from the classical colloid filtration theory (CFT) in the presence of repulsive DLVO interactions were investigated. The deposition behavior of uniform polystyrene latex colloids in columns packed with spherical soda-lime glass beads was systematically examined over a broad range of physicochemical conditions, whereby both the fluid-phase effluent particle concentration and the profile of retained particles were measured. Experiments conducted with three different-sized particles in a simple (1:1) electrolyte solution reveal the controlling influence of secondary minimum deposition on the deviation from CFT. To verify the validity of CFT in the absence of surface charge heterogeneities, two additional sets of experiments were conducted using solutions of high pH or containing anionic surfactant (sodium dodecyl sulfate). The results indicate

that both secondary minimum deposition and surface charge heterogeneities contribute significantly to the deviation from CFT generally observed in colloid deposition studies.

2-23

Particle Deposition onto Micro -patterned Charge Heterogeneous Substrates

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The effect of collector surface charge heterogeneity on particle deposition efficiency is theoretically investigated near a micro-patterned charged substrate under radial impinging jet flow conditions. The surface charge heterogeneity on the collector is modeled as concentric bands of positive and negative charges having specified width and pitch, providing alternating favorable and unfavorable deposition sites for the particles. The fluid velocity distribution for radial impinging jet flow is obtained numerically. Using this velocity distribution, particle trajectories, concentration distributions, deposition fluxes, and collector efficiencies are obtained. The periodic charge heterogeneity on the substrate engenders an oscillating particle trajectory near the collector. Due to the coupled effects of hydrodynamic and colloidal forces, a region at the leading edge of each favorable band on the collector becomes inaccessible for particle deposition, implying that the actual favorable area fraction of the collector is less than its nominal value. Utilizing the actual favorable area fraction of the collector, one can modify the patchwise charge heterogeneity model to calculate the collector deposition efficiency in impinging jet flow geometry. The results indicate that the particle trajectories and deposition efficiencies are increasingly affected by surface charge heterogeneity as one moves radially away from the stagnation point.

2-24

Capturing the Essence of Deposition Phenomena: Random Sequential Adsorption and Related Models

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Although it is often the first thing that comes to mind in describing adsorption and deposition phenomena, the Langmuir model usually provides a poor description of the deposition of macromolecules and colloidal particles on solid surfaces. The deposition process in these cases is often irreversible and, in order to obtain an accurate description, it is necessary to account for surface exclusion effects and the transport mechanism of the depositing particles to the interfacial region. It is the purpose of this talk to review the rather remarkable progress that has been made during the last fifteen years towards the goal of a quantitative description of adsorption/deposition processes on solid surfaces.

The paradigm for the recent advances is, unquestionably, the Random Sequential Adsorption (RSA) model. Originally conceived to describe the packing of coal, this model accurately describes the blocking effects of the pre-deposited particles in an irreversible deposition process. The structure of the deposited particle configuration differs fundamentally from an adsorbed equilibrium fluid, although the difference can be negligible at low to medium densities. The basic model and its predictions for a single component, mixtures, non-spherical particles and macromolecules undergoing post-adsorption conformational changes will be reviewed. We also show how it can describe adsorption on a heterogeneous surface (the Random Site Model). In view of its rather simplistic representation of the transport process, RSA describes a variety of experimental data with surprising accuracy. The reasons for this fortuitous result will be discussed.

Larger particles may be strongly influenced by gravity as they deposit and in this case a different model is required. For situations in which gravity plays a dominant role and the particle trajectories are deterministic, the Ballistic Deposition (BD) model is appropriate. A new feature that emerges in this model is the presence of connected clusters of particles, even at low surface coverages. Processes that are intermediate between BD and RSA, which may be characterized by a single parameter, can also be described.

2-25

Embedding of phospholipid vesicles into exponentially growing polyelectrolyte multilayers: A new way to surface immobilized nanoreservoirs and nanoreactors

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Polyelectrolyte multilayers (PEMs) appear more and more as versatile tools to functionalize solid liquid-interfaces. Indeed, proteins with their native conformation¹, DNA², and quantum dots³ have been embedded in such films. An other functionalization strategy consists in adsorbing covalently modified polyelectrolytes⁴ and also stimuli responsive and hydrolysable polyelectrolytes.⁵ In this communication we present a method to embed in tact (polyelectrolyte stabilized) phospholipid vesicles into PEMs. Two ways of deposition will be described : either by the dipping method⁶ or by spray pulverisation.⁷ The build up of the architectures was characterized by means of quartz crystal microbalance with dissipation, atomic force microscopy and ellipsometry. The molecular integrity of the vesicles was studied by encapsulation of $\text{Fe}(\text{CN})_6^{4-}$ into the vesicles before embedding and monitoring of the ferrocyanide release from the functionalized PEM by means of cyclic voltametry on the surface of gold electrodes. The spray pulverisation method offers the advantage of faster and easier deposition. We will also present the embedding of two stages of vesicles into the PEMs containing two kinds of encapsulated molecules.

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Preparation of self-assembled nanostructures using colloidal chemistry

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Nanomaterials offer a wide ranging novel applications encompassing electronics, materials sciences, medical sciences and engineering. However, many of these applications require an organization of such materials into various ordered structures. Self-assembly processes that are driven mainly by competing molecular interactions like hydrophobic versus hydrophilic components, gravitational, van der Waals or coulombic interactions, amongst others, have been shown to have the potential of achieving complex structures, from 0D to 3D. For that aim, basic contributions to the self-assembly phenomenon, such as particles-particles and particles-substrate interactions, capillary forces, particle diffusion, must be understood and controlled.

In the present work, silica and gold particles smaller than 100nm have been assembled in various ordered structures. Three-dimension colloidal crystals with ordering lengths of tens of μm have been obtained by drying highly concentrated silica suspensions on flat substrates or by using dip-coating. Two-dimensional ordered monolayers of nanoparticles have also been produced by evaporating the solvent of suspensions of adapted pH, ionic strength and particle concentration. Dip-coating

furthermore allowed the production of micrometers-long chains of particles with diameters between 50 and 15nm using topographically nanopatterned substrates, prepared by X-ray Interference Lithography which guides the assembly process. Substrates patterned with holes combined with dip-coating can lead to ordered arrays of single dots over tens of μm . The forces involved during both self-assembly and *guided*-assembly processes arise notably from dispersion, capillary and adhesion forces. Theoretical analyses based on existing models have been performed for each assembled system to establish the relative importance of these contributions as a function of the most relevant experimental parameters.

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Interpretation of the stability of water-in-oil emulsions based on adsorption phenomena at oil/water interface

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Adsorption of bituminous components from heptane/toluene mixtures at oil/water and oil/gold interfaces was measured in situ by a Quartz Crystal Microbalance. The adsorption kinetics follows two distinct regimes depending on bitumen concentration. At low concentration (<1.5wt%), an unsteady irreversible adsorption at oil/water interface manifests in the form of a slow and continuous build-up of asphaltenes with minor resins into multi-layers. At high concentration, a steady adsorption with limited reversibility is measured where saturation is reached after formation of a monolayer composed of asphaltenes with major resins. The concentration regimes are determined by the resin-to-asphaltene ratio in the bulk phase. The rigidity of oil-water interface at low bitumen concentration is related to the rigid network formed by sterically non-stabilized asphaltenes. In this regime, formation of asphaltene bridges between water drops destabilize the emulsions against flocculation, thus dewatering of bitumen froth is easy. However at high bitumen concentration, in the steady regime, water-in-oil emulsions are kinetically stabilized against flocculation by sterically stabilized asphaltene layers, and dewatering of bitumen froth becomes difficult.

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Anisotropic Adsorption of Molecular Assemblies on Inorganic Surfaces

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Oriented adsorption of rod-like molecular assemblies on inorganic surfaces is analyzed in terms of anisotropic van der Waals interactions between an assembly and the substrate.

The van der Waals interaction is calculated using a Lifshitz methodology using the anisotropic properties of the crystalline substrate derived from a first principles computation of the dielectric response function for graphite. It is shown that, provided the assembly is sufficiently large, a small amount of substrate anisotropy provides torque that overcomes rotational Brownian motion near the surface. The probability of a particular orientation is computed by solving a Smoluchowski equation that describes the balance between torque and Brownian forces. The results show that the torque aligns both cylindrical micelles and protein fibrils. In the systems studied here, the interaction energy is a minimum when the assembly lies perpendicular to a symmetry axis of a crystalline substrate. These results agree with experiments with both cylindrical and hemi-cylindrical micelles and proteins adsorbed on crystalline graphite.

Monoparticle films of gold nanorods formed at a liquid-liquid interface

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We have found that a monoparticle-film of gold nanorod (NRs) could be formed at a liquid-liquid interface of hexane and water. In this study, we characterized the optical properties of the monoparticle-films of NRs that were transferred onto glass substrates. In a phase-separated solution, 20 mL of the NRs solution and 10 mL of hexane, acetonitrile (5 mL) was vigorously injected. A monoparticle-film formed at the liquid-liquid interface was transferred onto a glass plate that was vertically lifted up through the interface.

Scanning electron microscopic images of the monoparticle-film of NRs showed that there are few stacked particles in the film. It is known that a NRs solution shows two clear absorption peaks in visible (~520 nm) and near-IR (~800 nm) regions; however, the spectra of the deposited films show no clear absorption peaks. The peak profiles of deposited films prepared from different concentrations of NR solutions were almost independent of the concentration of NRs. This indicates that the deposited NRs form two-dimensional aggregates on the substrates. Degree of the aggregation was changed by additional amphiphilic molecules, for example, phosphatidylcholine in acetonitrile.