

ORAL CONTRIBUTIONS

Coalescence behaviour of giant Pickering droplets and colloidosomes stabilised by poly(*tert*-butylaminoethyl methacrylate) microgel latexes.

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The coalescence of two oil droplets grown in the presence of lightly cross-linked 260 nm diameter charge-stabilized poly(*tert*-butylamino)ethyl methacrylate (PTBAEMA) latexes was monitored using a high-speed video camera as a function of the aqueous dispersion pH. Three model oils (*n*-dodecane, isopropyl myristate and sunflower oil) were investigated, each in the absence and presence of an oil-soluble cross-linker (tolylene 2,4-diisocyanate-terminated poly(propylene glycol), PPG-TDI). In the absence of PPG-TDI, rapid coalescence was observed for giant Pickering oil droplets, which exhibited faster coalescence times compared to bare oil droplets. An increase in the damping coefficients for coalescing Pickering droplets (compared to those of bare oil droplets) indicated PTBAEMA latex particle adsorption at pH 10.¹ Addition of PPG-TDI cross-linker to oil droplets in the absence of latex particles led to a reduction in the interfacial tension, confirming the surface-active nature of this reagent. PPG-TDI was added to the oil phase to react with the secondary amine groups on the PTBAEMA latex, producing giant colloidosomes that are stable to coalescence. This stability was not observed for bare oil droplets in the presence of PPG-TDI, confirming that the cross-linked particles at the interface provide the additional stability. Interactions between asymmetric droplets were also examined. The effect of adding oil-soluble cross-linker to only one *n*-dodecane droplet resulted in *arrested coalescence* in the presence of PTBAEMA latex particles (see Figure 1). Here the droplet aging time was found to be critical. Aging times of less than 60 s led to catastrophic droplet coalescence, whereas aging times longer than 60 s indicated cross-linker diffusion from one droplet to the other, which produced inter-crosslinked colloidosomes. Arrested coalescence was only observed for aging times of approximately 60 s. The overall coalescence behaviour at pH 10 was then compared to that of oil droplets grown in acidic aqueous solution in the presence of swollen microgel latex particles which were also found to adsorb at the oil-water interfaces.

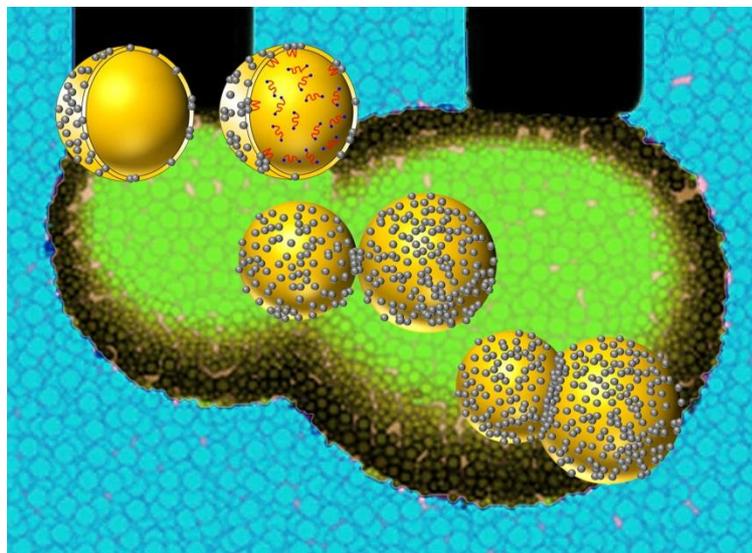


Figure 1. The arrested coalescence recorded for two *n*-dodecane droplets grown in the presence of a 1.6×10^{-2} wt % aqueous dispersion of 260 nm charge-stabilised PTBAEMA latex particles at pH 10 in the presence of 0.01 M KNO_3 . Initially, $0.1 \text{ mg} \cdot \text{mL}^{-1}$ PPG-TDI cross-linker was present in only the right hand droplet.

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OC002

Can an emulsion be effectively stabilized by highly hydrophilic nanoparticles?

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The stabilization of Pickering emulsion is commonly recognized as a result of large energy for solid particles to be removed from oil/water interfaces to either of bulk phases. This detachment energy rapidly falls to less 10 KT when the contact angle of the particles at the interfaces is lower than 20 degree. As such, highly hydrophilic particles cannot effectively stabilize emulsions. Here we demonstrate that when the electrostatic repulsion between charged particles and oil droplets is significantly reduced close to zero by varying the dispersion pH, the particles can effectively and efficiently stabilize oil-in-water emulsions; the emulsions can remain stable for several months. This works not only for silica particles with sizes ranging from 15 nm to 250 nm, stabilized with and without lysine, but also for 14 nm gold nanoparticles stabilized by citrate. According to our current experimental data, we attribute this unusual emulsion stabilization by highly hydrophilic particles to the Van der Waals attractive energy between oil droplets and the particle ensembles enclosing the droplets. This is very different from classic Pickering emulsion stabilization, which is determined dominantly by the surface wetting energy of solid particles, and thus opens up a new mechanism for emulsion stabilization.

OC003

Destabilising Pickering Emulsions by Drop Flocculation and Adhesion

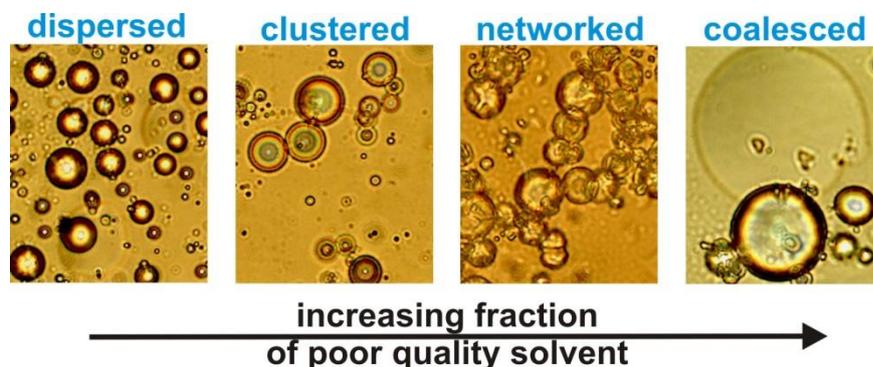
Catherine Whitby, Hunainah Khairul Anwar, James Hughes

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The focus of this presentation is on destabilisation in particle-stabilised (Pickering) emulsions. These emulsions are kinetically stabilised by particles attached to the drop surfaces. Particles assemble in layered structures at liquid interfaces. The layers behave like solids on length scales larger than the particles, but remain fluid in the pore spaces between the particles.¹ Controlling the interactions between the particles is critical to emulsion stability.² Briggs³ and Lucassen Reynders and van den Tempel⁴ first observed that weakly flocculated particles are most efficient at (kinetically) stabilising emulsions. We have explored the mechanism by which further aggregation of particles leads to emulsion destabilisation.

We investigated the role of particle flocculation in the destabilisation in emulsions of water drops coated by organoclay particles in organic solvents. We found that the stability of the thin films between the drops depends on the interactions between the interfacial layers of particles. The drops are well dispersed in solvent mixtures that contain low fractions of poor quality solvent for the clay particles. Reducing the quality of the solvent for the organoclay particles increases the attractive interactions between the layers. As the fraction of poor quality solvent increases, the drops adhere together into clusters and networks. The drops coalesce in poor quality solvents.

Our major finding is that emulsions destabilise under conditions where the energy of adhesion between the layers is comparable to the energy required to detach the particles from the drops. The particle layers rupture and the particles aggregate together. The uncoated water drops coalesce and separate out of the emulsion.



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OC004

Collection of fine particles by a water droplet under an applied electric field.

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The transport of dry solid particles from the gas phase to a liquid interface is pertinent to a number of emerging applications such as “liquid marbles” and so-called “dry water”. Whether particles attach to the interface, remain at the interface, or are completely engulfed by the liquid, significantly influences their utility for a particular function. Here we report on experiments where the transport of dry particles to a pendent water droplet is driven by an applied electric field. A bed of dry particles is placed on a charging plate and positioned beneath the pendent droplet. Either the separation distance is decreased while maintaining a constant voltage, or the voltage is increased at a fixed separation, until particles “jump” to the droplet and their charge is allowed to flow to earth.

The transport of particles of silica (diameter 80 – 170 microns), poly(methyl methacrylate) (PMMA, diameter 102 microns), and base metal sulphides (pyrite, sphalerite and galena) and their mixtures, to a 7 mL water droplet has been studied. A critical applied voltage was required to initiate transfer of silica particles, at which point an extremely rapid transfer of a large number of particles occurred [Liyanaarachchi et al. 2013. *App.Phys.Lett.* 103, 054105]. This “avalanche” usually resulted in detachment of the droplet due to the increased weight of engulfed particles. The rate of increase of the voltage determined the magnitude of the required critical voltage; the more rapid the voltage increase the higher the critical voltage. In some instances the water droplet deformed, due to the applied electric field, and contacted the particle bed directly. This led to partial discharge of the electrostatic charge in the bed, and the droplet was observed to rebound from the bed and oscillate for a number of seconds.

When mixed with silica particles, samples of 10 and 20 wt% PMMA underwent avalanches in the same manner as pure silica particles. Mixtures of 30 wt% PMMA were observed to undergo a number of transfer events as the voltage increased, with small numbers of particles transported in each instance. When the PMMA content in the mixture was 50 wt% or higher no avalanche occurred. Optical images of the mixtures indicate the silica particles coat the PMMA particles, and that the degree of coating determines whether the system avalanches or not. An admixture of metal sulphide particles to the silica appears to provide a moderating effect to the particle transfer. This offers the intriguing possibility to design and prepare powder coatings for liquids with a range of physico-chemical properties, and to apply the coatings in a simple manner that may be readily scaled-up.

OC005

Lifetime of Surface Nanodroplets and Surface Nanobubbles

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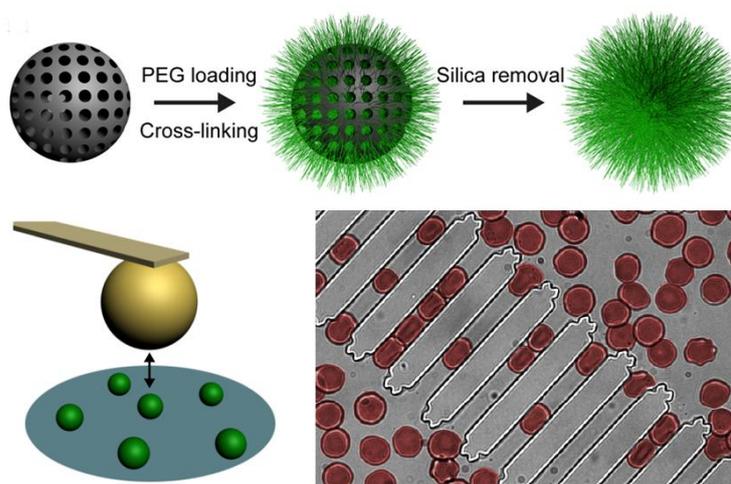
Surface nanodroplets are nanoscopic droplets (e.g. of oil) on (hydrophobic) substrates immersed in water. Correspondingly, surface nanobubbles are nanoscopic gaseous domains on water-immersed substrates. Both can form through local oversaturation of the water with oil or gas, respectively. Such local oversaturation can be achieved through solvent exchange. Here we study the lifetime of such surface nanodroplets, showing how they dissolve over time. We highlight pinning effect, which considerably extend the lifetime of both surface nanodroplets and nanobubbles and reveal stick-slip motion of the three phase contact line during the dissolution process. We also discuss collective effects, which extend the lifetime too.

Engineering of PEG Particles for Mimicry of Red Blood Cells in a Microfluidic Device

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Polymer carriers with finely controlled properties have been receiving great interest in therapeutic delivery systems for biomedical applications [1]. Recently, we have developed a robust approach for preparing polymer replica particles using a mesoporous silica (MS) templating method, where the template is removed following polymer infiltration and cross-linking [2]. This versatile method has been used to prepare particles of different size, shape, chemical composition, and elasticity, which have the capacity for both cargo encapsulation and delivery [3]. Microfluidic devices have been



recently used to mimic *in vivo* environments for studying the biological behavior of engineered particles [4]. Herein, we report the engineering of poly(ethylene glycol) (PEG) hydrogel particles with tunable elasticity and investigate their deformability in a microfluidic blood capillary model. The hydrogel particles were fabricated with PEG via the MS templating method [5]. The elasticity of the PEG particles was controlled by tailoring the cross-linking density and was characterized by colloidal-probe atomic force microscopy. The obtained PEG particles were super-soft with a tunable Young's modulus (E_Y) as low as 0.2 kPa, which is 40-fold lower compared to previously reported hydrogel particles, as well as 130-fold lower compared to red blood cells (RBCs). To investigate the deformability of the PEG particles, a microfluidic blood capillary model was designed to mimic dimensions and pressure differentials of the *in vivo* environment. It was found that the PEG particles with lower cross-linking density could pass through microchannels, mimicking the behavior of human RBCs. The reported PEG particles represent a new generation of soft hydrogel particles for investigating particle behavior in biological environments, which have the potential to provide new insights for the design and development of improved drug delivery carriers for biomedical applications.

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Non-powered Low-cost Surface Capillary Microfluidic Device with High Sample Transport Efficiency

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In this study we investigate the liquid sample delivery speed and efficiency of microfluidic channels for low-cost and low volume diagnostic devices driven only by capillary force. We select open, non-porous surface grooves with V-shaped cross section for modeling study and for sensor design. We quantitatively analyze the liquid wicking speed in V-grooves by using a proposed model of Rye et al. This analysis is used to generate data for design of sensors. By combining V-groove channels and printable paper-like porous detection zones, microfluidic diagnostic sensors can be formed. Suitably long surface V-grooves allow short liquid transport time (< than 500 ms), thus reducing the evaporation loss of the sample during transport. Non-porous V-grooves also significantly reduce chromatographic loss of the sample during transport, therefore increasing the sample delivering efficiency. Sensors of such design are capable of conducting semi-quantitative chemical and biochemical analysis (i.e. with a calibration curve) with less than 1000 nL of samples and indicator solution in total.

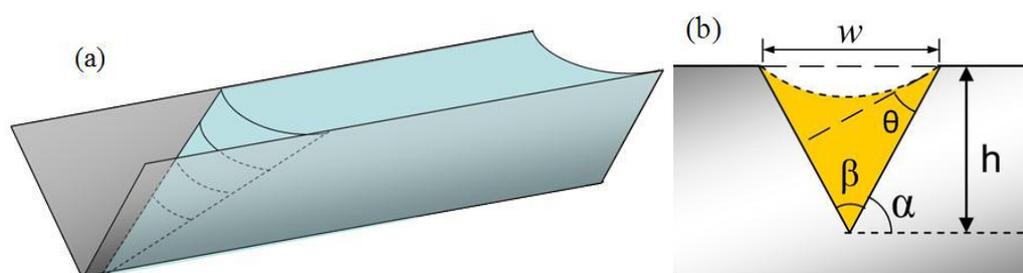


Fig. 1: (a) A schematic showing the geometry of a liquid wicking front in a V-groove; (b) modeling parameters of capillary flow in a V-groove

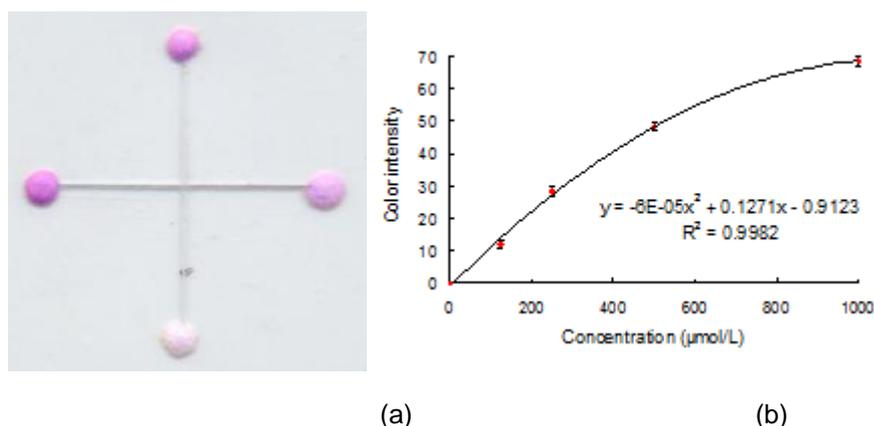


Fig. 2: (a) The scanned image of a four-zone V-groove microfluidic device in which a series of standard NO₂ – solutions were used to construct a calibration curve. (b) A calibration curve constructed using the colour intensity readings of the four zones. Six repeated measurements using six sensors gave the error bars.

OC008

Volatile Fluorinated Nanoemulsions: Using Colloid Science for Controlled Delivery of Inhalation Anaesthesia

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Inhalation anaesthesia represents an area in which there has been little chemistry based development for many years. Currently, safe and accurate anesthesia delivery is reliant on large, complex and expensive machines operated by very specialized, highly trained personnel, all of which factors limit their use outside of modern clinical settings. A simpler, safer and cheaper delivery system, with equivalent performance, could provide an alternative means of anesthesia delivery in challenging situations, such as pre-hospital medicine, in-the-field anesthesia, warfare anesthesia and in the challenging conditions often encountered in developing countries, where access to safe anesthesia can be limited by a shortage of trained staff, and compromised by failure of complex equipment.

Here we present a proof of concept for a dispersion based anaesthetic delivery device. Novel dispersions of the volatile inhalation anaesthetic sevoflurane have been formulated that can provide controlled, sustainable release of anaesthetic over clinically useful timescales. The emulsions can be simply formed with manual shaking, reproducibly yielding droplets within the nanoemulsion range. Using a custom flow-rig, release of anaesthetic gas from the emulsion has been evaluated, and clinically useful levels achieved, maintained and controlled through appropriate stirring of the formulation.

Once some essential factors are taken into account relating to the unusual nature of the fluorinated systems and the highly perturbed environment of their evaluation, the observed behaviour regarding sevoflurane evaporation can be reasonably well explained by existing theoretical models of evaporation from emulsions and links between release and emulsion structure defined, providing the basis for future development.

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Paul A, Wilkes A, Salama I, Goodwin I, Hall JE, British Journal of Anaesthesia. 2014; 112(1): 189-190P

OC009

Self-Assembly of Nanoparticle Surfactants and their use as Theranostic Agents

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Controlling the assembly of nanoparticle building blocks is of great interest because 'emergent' properties arise that can enable new applications in energy, imaging and medicine. Self-assembly has long been demonstrated a viable approach to drive bottom-up organization in amphiphilic systems including molecular surfactants and block-copolymers. We have recently synthesized nanoparticle surfactants that also self-assemble and cluster into 'colloidal-molecules' with controllable morphology. A scalable synthesis method was developed by tuning steric stabilization imparted by grafted hydrophilic polymers and short-ranged attractive interactions from small molecule ligands. The phase behavior of nanoparticle surfactants has been explored in detail and found to mimic that of molecular surfactants. Cluster formation is analogous to micelle formation and nanoparticle surfactants also stabilize oil-water and air-water interfaces by adsorbing strongly. The close arrangement of metallic particles in clusters and emulsions induce changes in optical absorption and local electric fields due to surface plasmon resonance. Specifically, near infrared (NIR) absorption is greatly enhanced in nano-Pickering emulsions. This enables the use of these materials as powerful non-linear contrast agents for photoacoustic imaging and for mechanical thrombolysis. Self-assembly of surfactant nanoparticles represents a powerful platform to form diverse nanostructures and colloidal materials with novel properties.

OC010

Self-assembled Monolayers on Silicon Based on Halogen Bonding

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The halogen bond is a strong non-covalent bond that, similarly to the hydrogen bond, leads to the formation of stable adducts in solution. Here, for the first time, we demonstrate that long-chain iodo-perfluorinated alkanes adsorb from solution onto silicon and silicon nitride surfaces and form stable and compact monolayer films. The specific interaction of surface oxides and nitrides towards the Lewis acid iodine make it possible to vary the structure of the terminal groups, and thus permit the introduction of a great range of functional groups onto a surface. Studies of the wettability of the monolayers, of their composition using X-ray photoelectron spectroscopy (XPS), and of their thickness by X-ray reflectometry indicate that the monolayers are stable in most aprotic solvents. The semi-covalent adsorption of iodo-perfluorinated alkanes produces hydrophobic surfaces with extremely low free energy (16 mJ/m^2). We used contact angle measurements and optical ellipsometry to study the kinetics of adsorption of monolayer films and to examine the experimental conditions necessary for the formation of high-quality films. The

monolayers appear to be stable at room temperature but their constituents desorb when wetted by protic solvents, which compete through hydrogen bonding to the halogen bonding. This new family of self-assembled monolayer could find ideal application in the electronic field, where use of protic solvents is deleterious for high efficiency.

OC011

Surface Tension of Ionic Liquids and Wetting Behaviour on Polymer Surfaces

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Ionic liquids have surface tensions intermediate between those of alkanes (van der Waals interactions only) and water (including strong hydrogen-bonding). Both cations and anions of the ionic liquid contribute to the surface tension through their chemical structure. Longer alkyl chains in particular, behave like the tail of a classic surfactant: they try to escape the polar environment of the bulk ionic liquid. In that sense, ionic liquids behave like organic solvents. On the other hand the relation between surface tension and molecular volume of the ion pair resembles that found for molten salts. A relation is established between the surface tension of ionic liquids and their polarity parameter π^* .

The wetting behaviour of ionic liquids on three chemically different polymer surfaces is identical to that of common organic solvents as well as ethanol-water mixtures. This confirms that, in the absence of chemical reactions and surfactants, the contact angles on any chemically inert surface fall on the same master curve. It also validates the empirical approach, due to Zisman, which consists in plotting the cosine of the advancing contact angle versus the surface tension of the probe liquids and then extrapolating the linear part of the dependence to complete wetting (zero contact angle) in order to obtain the critical surface tension of wetting. Given the intensive research in ionic liquids we expect these to become increasingly used for contact-angle based surface characterisation of polymer surfaces.

OC012

Secondary Spreading of Evaporating Drops

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There are many instances when small reactive droplets are in contact with metal surfaces (e.g. sea spray, condensation on aircraft wings) and understanding their behaviour is important to reducing the impact of resultant corrosion. When a small corrosive droplet is placed on a metal surface it will spread, then pin and progressively evaporate. In some cases, after some significant delay the spreading recommences. This secondary spreading can be quite extensive (covering a surface area up to 2-3 times the original footprint of the droplet) depending on the reactivity of the metal-droplet contact area. Other researchers have observed the process with highly reactive metals such as zinc and magnesium and we have documented similar behaviour on mild steel and aluminium. We investigated this phenomenon with several solid-liquid combinations and as a function of the pH inside the droplet. It is clear from our experiments that evaporation has to reach a rather advanced stage before secondary spreading occurs. However the effect is seen only for highly reactive pairs like concentrated sulphuric acid on mild steel or concentrated sodium hydroxide on aluminium. We discuss the mechanisms of secondary spreading in view of limiting the extensive corrosion damage.

OC013

Phase inversions of dispersed systems of air and liquids stabilized by particles

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Dispersed systems consisting of fluids, such as emulsions of oils and water, are stabilized by colloidal particles. The particles are adsorbed at fluid interfaces, forming adsorbed films which suppress coalescence and disproportionation of droplets. One of the most crucial parameter in preparing particle-stabilized dispersed systems is wettability of particulate materials at fluid interfaces.

Dispersed systems consisting of air and liquids can be stabilized using particulate materials¹⁻³. It has been shown that relatively liquid-philic particles preferably stabilize air-in-liquid (A/L) materials, that is, foams, while relatively liquid-phobic particles form liquid-in-air (L/A) materials. Dry liquids are one of the representatives of the L/A materials. The dry liquids consist of micron-sized liquid droplets covered by adsorbed particle films and behave like free-flowing powder.

We have controlled wettability of intrinsically hydrophobic fumed silica particles by mixing water and ethylene glycol (EG). The silica particles are relatively liquid-phobic when the water content is high, while they behave relatively liquid-philic when the water content is low. The phase inversion from dry liquids to foams is induced by increasing EG content at a fixed volume fraction of liquid relative to total volume (ϕ_L). Another type of phase inversions is also induced by controlling ϕ_L at a fixed water content. A diagram regarding types of dispersed systems of air and liquids has been constructed, showing the types of materials are dependent on both particle wettability and ϕ_L , along with particle-stabilized emulsions.

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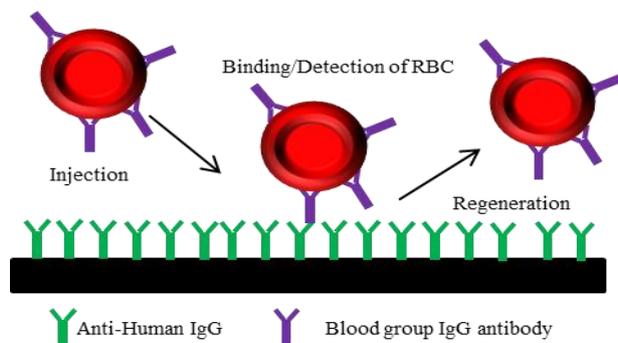
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Multi-Functional Platform for Blood Group Phenotyping using Surface Plasmon Resonance

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Accurate and reliable phenotyping of blood groups is of the utmost importance prior to transfusion. Mismatching of incompatible donor and patient blood types could potentially lead to a haemolytic transfusion reaction, which can be fatal. Currently, there are many well established blood typing methods available, such as the column agglutination test (CAT), however methods quantifying these antibody-antigen interactions are limited. This is particularly important to identify and characterize weak interactions between weak subgroup variants, which are often difficult to determine by the naked eye and have the potential to be overlooked. The biosensing system, BIAcore, relies on surface plasmon resonance (SPR) detection to quantify interactions between biomolecules. Previous studies have shown the use of SPR for blood group antigen detection [1] and antibody detection [2-3], however, these methods showed poor regeneration and loss of functionality after a single use due to the inability to fully desorb bound material. Each chip was also limited to a single blood group. A fully regenerable, multi-functional platform for quantitative blood group phenotyping via SPR detection can be achieved by covalently immobilizing an antibody, anti-human IgG, to the chip surface. Anti-human IgG is able to recognize and bind to the Fc region of human IgG antibodies for detection (Fig.). The surface can therefore be used as an interchangeable platform capable of quantifying the blood group phenotyping interactions between RBCs and IgG antibodies. Much like the Indirect Antiglobulin Test (IAT) used to detect blood groups using IgG antibodies with the CAT, the blood group IgG antibody is incubated with RBCs, and the cells become sensitized, which allows them to bind to the anti-human IgG on the chip surface. This test has potential to quantitatively detect any blood group with a corresponding IgG antibody. A clear distinction between positive and negative results has been achieved using anti-D IgG and reagent red cells, as well as complete regeneration of the anti-human IgG surface. Very little degradation, if any, of the immobilized surface has been observed after over 100 regenerations. Consecutive testing of different blood types has also been successful, allowing multiple blood groups to be detected using a single chip. This multi-functional platform presents potential for quantifying antibody-antigen interactions for blood group phenotyping.



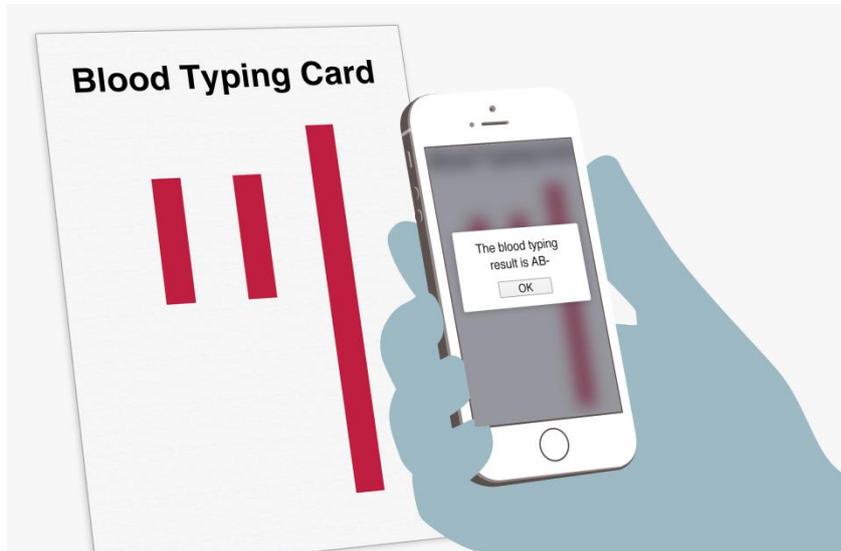
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OC015

Barcode-like Paper Sensor for Smartphone Diagnostics: An application of Blood Typing

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This work introduced a barcode-like design into paper-based blood typing device by integrating with smartphone-based technology. The concept of presenting paper-based blood typing assay in a barcode-like pattern significantly enhanced the adaptability of the assay to the smartphone technology. The fabrication of this device involved the use of printing technique to define hydrophilic bar channels which were respectively treated with Anti-A, -B and -D antibodies. These channels were then used to perform blood typing assays by introducing a blood sample. Blood type can be visually identified from eluting lengths in bar channels. A smartphone-based analytical application was designed to read the bar channels, analogous to scanning a barcode, interpret this information and then report results to users. The proposed paper-based blood typing device is rapidly read by smartphones and easy for the user to operate. We envisage that the adaptation of paper-based devices to the widely accepted smartphone technology will increase the capability of paper-based diagnostics with rapid assay result interpretation, data storage and transmission.

Multistage Porous Silicon Nanovectors for Cancer Theranostics

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Over the past decade, the progress of material synthesis and the rise of nanotechnology have made possible the production of nanomaterials with tailored properties and specific functions. The development of nanotechnology in the biological area has opened new possibilities in the design of new platforms for target-specific delivery of therapeutic or imaging agents [1].

Porous silicon (pSi) particles have emerged as effective delivery carriers, due to their high surface area, tuneable size and shape, biocompatibility and relatively simple surface functionalisation [2]. These types of nanomaterials can easily integrate more than one kind of imaging or therapeutic agents, converting them into potential multifunctional nanoplatforms to be used for cancer theranostics [3]. We have recently developed a new synthetic pathway to fabricate size and shape-controlled pSi nanoparticles, which have been proved to be biodegradable, to have high loading capacities and to be functionalisable with targeting moieties. These nanomaterials can also be used for multimodal cancer treatments, for example combining effective chemotherapy treatments and hyperthermic therapy [4]. In this regard, gold nanoparticles have proven to be excellent non-invasive means of heating tumour cells in radiofrequency and microwave fields [5]. By loading both gold nanoparticles and chemotherapeutics drugs into porous silicon nanoparticles, a combination of hyperthermia and chemotherapy treatments can be exploited. Both, loading and release of the therapeutic payload can be tuned by the surface modification of the porous nanocarrier, which provides an improved and more targeted delivery exclusively in the tumour tissues.

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OC017

Thermochemistry of the Hydrophobic Effect – O/W Emulsions

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Water and oil do not mix. This essential statement of the hydrophobic effect explains why oil-in-water (O/W) emulsions are unstable and why energy must be supplied to form such emulsions. Breaking O/W emulsions is an exothermic event. Yet metastable O/W emulsions can be prepared with only water acting as a surfactant. The emulsions are stabilised by adsorption of hydroxide ions formed from the enhanced autolysis of interfacial water.

These hydroxide-charged emulsions provide a particular advantage for the investigation of the energetics of emulsion stability – when the emulsion is broken by the addition of acid to neutralise the stabilising hydroxide ions, the neutralised surfactant is water, there is no other released surfactant whose solution properties need to be considered.

There are only three significant contributions to the heat of reaction when a hydroxide-stabilised O/W emulsion is broken by addition of acid: the desorption and then neutralization of the surface hydroxide ions and the release of the interfacial tension. Two of these terms can be assessed independently – the heat of neutralization of the hydroxide ions is obtained from the quantity of the adsorbed hydroxide measured in the emulsification process, or the surface charge density times the surface area, together with the well-known heat of reaction of a strong acid with a strong base (-56 kJ mol^{-1}). The interfacial tension term is calculated from the measured size of the emulsion drops and the interfacial tension of the oil. The heat of desorption of the hydroxide ions from the oil/water interface is not directly accessible, but can be obtained from the difference between the overall measured heat of reaction and the sum of the two terms described above. This experimental value can then be compared to the theoretical estimate made from the fluctuation/correlation model of the hydrophobic force (Gray-Weale & Beattie, PCCP 2009 11, 10994). Excellent agreement is found. Hence the measured heat provides a direct test of the allegedly controversial role of the hydroxide ion in stabilizing the O/W emulsions and a quantitative measure of the fundamental hydrophobic effect.

OC018

Harvesting Water from Air: Micro-Patterned Polymer Surfaces for Water Capture and Heat Transfer

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The idea of condensing and collecting atmospheric water originated from the observation of the Namib Desert beetle capturing fog as a source of drinking water in its arid environment [1]. The topographically and chemically patterned elytra of this desert beetle concentrates water droplet nucleation and growth on hydrophilic micron scale bumps and facilitates liquid removal of the large unstable droplets through hydrophobic troughs. Biomimetic surfaces designed to replicate this structure have been produced by etching methods [2-4]; however these are limited to the lab scale due to expense and complexity.

We have previously described a simple synthetic procedure that relies on dewetting hydrophilic poly (4-vinylpyridine) (P4VP) thin films on hydrophobic polystyrene (PS) layers, to yield a surface with micro-scale hydrophilic bumps lying atop a hydrophobic matrix [5]. This surface was found to be effective in collecting substantial amounts of water ($\sim 3 \text{ L/m}^2 \text{ hour}$) and is composed of inexpensive materials. The surface is readily up scalable due to the spontaneous nature of dewetting and the ease of preparing polymer bilayers.

To date, the measure of water collection efficiency has relied solely on the mass of water collected off a cooled surface when placed adjacent to a humid air stream. We have designed a new controlled condensation environment, a shell and tube condenser system, to test the water collecting performance of our micro-patterned surfaces against alternatives [4]. We measure two variables: heat transfer due to condensation and the mass of condensed water collected. This information is then correlated with early time droplet nucleation and growth data obtained by optical microscopy to provide a holistic picture of the nucleation, growth, coalescence and roll-off of droplets on each surface. We applied this system to identify the effect of size and density of surface features and wettability contrast on water collection performance efficiency. This systematic and robust approach provides a more reliable result when comparing surface condensation and water collection efficiency compared to existing experimental methods. This method of testing also minimises errors due to external factors and shows that micro patterning increases the heat transfer efficiency of surfaces in condensation applications.

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OC019

Understanding Macroscopic Adhesive Strength based on Single Molecule Energy Landscapes

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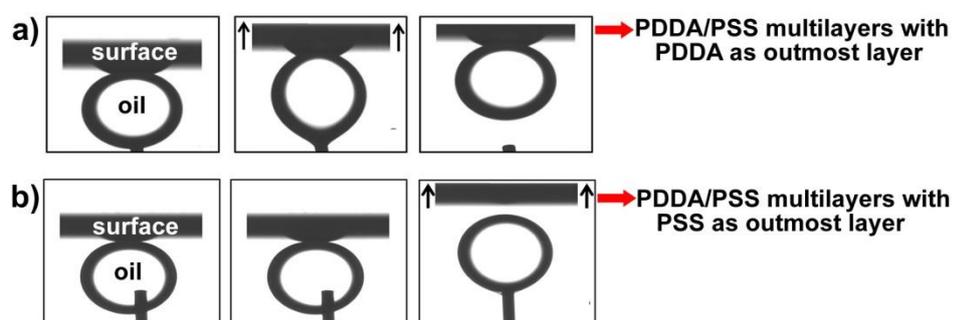
Unraveling the complexity of the macroscopic world based on molecular level details relies on understanding the scaling of single molecule interactions towards integral interactions at the meso- and macroscopic scale. Here, we discuss how one can decipher the scaling of individual single acid-amine interactions towards the macroscopic level, where a large number of these bonds interacts simultaneously, using a synergistic experimental approach combining Surface Forces Apparatus (SFA) experiments and single molecule force spectroscopy (SMFS). We show that equilibrium SFA measurements scale linearly with the number density of acid-base bonds at an interface, providing acid-amine interaction energies of 10.9 ± 0.2 kT. Using Bell-Evans theory together with a non-equilibrium work theorem, we show how a set of single molecule interaction forces measured by SMFS similarly converges to an interaction energy of 11 ± 1 kT, with unbinding energy barriers of 25 kT \pm 5 kT. We will discuss in detail, how single molecule unbinding energy landscapes can be utilized to predict scenarios where a large number of molecules simultaneously interact, giving rise to both macroscopic equilibrated and non-equilibrated interaction energies during adhesive failure. Finally, we will also show how other specific adhesive bonds such as the Amine/Gold binding can be successfully studied in the context of our approach. As such, our experimental strategy provides a unique framework for molecular design of novel functional materials through predicting of large-scale properties such as adhesion, self-assembly or cell-substrate interactions based on single molecule energy landscapes.

Ion-Specific Oil Repellency of Polyelectrolyte Multilayers in water: Insight to charged Surface Hydration

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The hydration and wettability of charged surfaces are crucial in many peculiar surface functions such as lubrication, anti-fouling and self-cleaning [1]. How the nature of ionic groups affects the hydration and thus the wettability of charged surfaces, however, remains an open question. Herein, polyelectrolyte multilayer (PEM) films, made via layer-by-layer (LbL) assembly [2] of polydiallyldimethylammonium chloride (PDDA) and poly(styrene sulfonate) (PSS), are taken as models to study the effects of ionic groups on surface hydration and wettability. The X-ray photoelectron spectroscopy (XPS) measurements indicates that PDDA/PSS multilayer films have outmost-layer-dependent surface component, where charged quaternized amine ($-R_2N(CH_3)_2^+$) groups dominate at the surface when PDDA as outmost layer, while sulfonate ($-PhSO_3^-$) groups dominate when PSS as the outmost layer. Interestingly, outmost layer dependent surface wetting behavior of PDDA/PSS multilayers was observed. Although the water-in-air wettability shows little difference for the PDDA/PSS multilayers with different outmost layers, they behave quite differently for the oil-in-water wettability. The PDDA/PSS multilayers with PSS as outmost layer exhibit perfect underwater oil repellency, while those with PDDA as outmost layer show high affinity for oil adhesion atop, revealing different surface hydration properties of the $-R_2N(CH_3)_2^+$ and $-PhSO_3^-$ groups. Sum frequency generation spectroscopy (SFG) measurements of the PDDA/PSS multilayers indicates that the molecular conformation and orientation of $-R_2N(CH_3)_2^+$ and $-PhSO_3^-$ groups at the interface are responsible for their different surface hydration properties. Additionally, taking use of the perfect underwater oil repellency of PDDA/PSS multilayers with PSS as outmost layer, high-flux oil/water separation was successfully implemented through the PEM coated stainless steel meshes.



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OC021

Surface Hydrophobicity Increase Associated with Antibody Denaturation on Solid Surfaces

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Currently, the common method for measuring antibody denaturation is performed multiplexed assays based on the biochemical reaction¹. Few physical variables have been confirmed to associate with antibody denaturation. In this study, we have successfully confirmed that another physical variable – substrate surface hydrophobicity - was increased associated with antibody denaturation on the substrates. In the first part of this work, a systematic study of human blood grouping antibody longevity was carried out on paper and glass as substrates. Substrate surface hydrophobicity was characterized with contact angle instrument, which recorded as water contact angle on glass surface and water penetration time into the paper. Our results showed a clear correlation of an increase in substrate surface hydrophobicity and a decrease in antibody bioactivity of both substrates. In the second part of this work, an antibody fractal pattern was observed on glass substrate. As the antibodies lost their activities, the fractal patterns underwent a distinct and reproducible change. This suggests that a fractal pattern may be capable of predicting the bioactivity of antibody on glass substrate. Findings of this work generate new revenue of understanding the antibody denaturation on a given solid substrate, providing the scientific support for optimizing the sensor design and the commercial product design.

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A Paper based Zinc oxide nanorods Platform for Pre-concentration of Cardiac Biomarkers

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Biomarkers play significant role in the detection of various diseases. Biomarker is a characteristic that is objectively measured and evaluated as an indicator of normal biological processes, pathogenic processes, or pharmacologic responses to a therapeutic intervention. Biomolecules such as troponin, myoglobin and FABP serve as markers for cardiac diagnosis. Cheap paper based diagnostics and pre-concentration could serve as a striking substitute for analysis and separation of various blood components. The sensitivity and accuracy of the paper based system could be enhanced by few modification steps such as colloids engineering, functionalization with nanoparticles and bioactive paper surface engineering. ZnO nanostructure containing paper could provide a suitable platform for development of a high performance pre-concentrator for cardiac biomarkers as well as for biosensors due to their unique fundamental material properties [1]. These properties of ZnO nanostructures outlined in [2] are utilised in this application for designing a paper based pre-concentrator. In the present study the implementation is achieved based on hydrothermal synthesis of zinc oxide nanorods on paper in order to develop a paper based preconcentration module for cardiac biomarkers. Growth of nanorods in the laboratory atmosphere was done with extensive studies to achieve repeatability and structure optimization. Our optimized process offers production of a large quantity of ZnO nanorods on Whatman filter paper at a relatively high purity, high aspect ratio and low cost. Growth has been confirmed by using various characterization techniques. After synthesis of nanorods on the paper surface, the nanorods surface was modified by silanization for antibodies immobilization. Antibodies (Human IgG) were successfully immobilised on such a modified paper. Antigen (FITC-antiHIgG) was allowed to bind on the surface and now the next step is to release the bound antigen by breaking the antibody-antigen complex, which is require for preconcentration purposes [3]. Bound antigen was eluted using elution buffer with appropriate molarity. Eluate concentration was observed using spectrofluorometry and ELISA reader.

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OC023

Control of antibody immobilization density for selective capture of *P. falciparum* HRP2 protein in a multiplexed format from live mice, via a wearable skin patch

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The efficient and pain-free collection of circulating body fluid samples from people is becoming recognized as a key bottleneck in the development of the next generation of user-friendly diagnostic assays and devices.¹ In contrast, significant emphasis has been placed on downstream diagnostic activities, including assay chemistry and detection methods. However, relatively few of these novel techniques have become available where they are needed most – at the bedside, the outpatient clinic, the home or at remote locations. Alternative sampling technologies that combine aspects of sampling, biomarker capture/enrichment and detection have the potential to address these issues for a number of applications for which validated biomarkers (or panels thereof) are already available.

Microprojection arrays (MPAs) can be applied to the skin such that projections penetrate into the richly perfused dermal tissue fluid for selective capture and enrichment of circulating biomarkers. While we have recently demonstrated selective capture of several biomarkers from the skin of live mice, with different project geometries and application times,² the key challenge is developing suitable surface chemistries for efficient capture. Specifically, while numerous surface modification strategies have been developed for *in vitro* diagnostic applications, it is unclear how well these methods translate to the *in vivo* case. For typical *in vitro* methods (e.g. ELISA), extracted biomarkers are typically diluted into buffered solutions, where the capture chemistry occurs under controlled conditions (temperature, ionic strength, etc.), however in the *in vivo* case the only aspect that can be controlled directly is the surface chemistry.

Herein we report recent progress in improving the detection limit of a circulating biomarker both *in vitro* and *in vivo*, simply by optimizing the solution conditions for the antibody probe immobilization chemistry onto anti-fouling PEG surface. We found that maximizing the antibody density, independent of starting concentration, improved the detection limit of the assay by ~100-fold *in vitro*. The high antibody density surfaces also showed increase capture efficiency and improved detection limit *in vivo*. Finally, we applied MPAs functionalised with antibodies against both PfHRP2 and total IgG, in a multiplexed format, in order to measure both the target analyte along with an internal control for penetration.

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OC025

Covalently linking two dissimilar nanoparticles

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If nanoparticles are the basic building blocks of complex nanoarchitectures, nanoparticle hetero-dimers made out of separate and individual particles represent the first level of sophistication. Despite the fact that high-quality nanocrystals of almost any inorganic material can be synthesised since the beginning of this millennium, the preparation of simple hetero-dimers, consisting of two dissimilar nanoparticles and linked by at least one covalent bond, has not been achieved yet. Unlike the seeded-growth method, where one type of nanocrystal is grown on top of another, the method presented here is generic and does not require any fundamental compatibility between the two types of nanoparticles.

Our method is based on a two-step approach: in the first step, the two types of nanoparticles are mono-functionalised, which means they bear functionality in just one spot of their surface. The hetero-dimerisation is then being undertaken in a second step. Particles have been mono-functionalised by attaching them covalently to a solid support, passivating their surface and subsequent cleavage of the linker between particles and solid support. Then, two types of nanoparticles having been functionalised with different functional groups were finally dimerised. In this presentation, we will show the new synthesis method and examples for the hetero-dimerisation of dissimilar nanocrystals.

Nanoparticle hetero-dimers may be used for multi-modal bioimaging, solar energy conversion or other applications where multi-functional materials are required.

OC026

In-situ Synthesis of AuNP-CNF Nanocomposite in CNF colloidal suspension and its application

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Cellulose nanofibre (CNF) is becoming a popular natural nanomaterial, as its large surface area, high Young's modulus, good thermal and chemical stability, as well as low-cost and large abundance in natural resources. CNF is very easy to disperse in water and forms a colloidal suspension. This work reports an in-situ synthesis of gold nanoparticle (AuNP)-CNF nanocomposite in a one-pot process in CNF colloidal suspension, as well as the application of the nanocomposite in building localized conductive zones on surfaces. In CNF colloidal suspension, charged interfaces on CNF create a number of "growing points" for particle in-situ synthesis and growth. In this way, particles can be tightly bound to nanofibre surface, and the growth of the AuNPs can be well controlled by reaction conditions in CNF suspensions easily. The obtained AuNPs-CNF nanocomposite has combined the advantages of both AuNPs and CNF, such as conductivity and large surface area. Here, we also report one application of the nanocomposite in building the localized conductive surfaces on other substrates, which can be paper, plastic, glass or rubber, etc. On the localized conductive zones on glass surface, we demonstrated the great advantages in one of the possible applications - surface enhanced Raman spectroscopy.

OC027

Relaxation NMR Studies of Nano-structured Carbon Materials

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Solvent relaxation NMR has been used to estimate the surface areas and wettability of various types of nanostructured carbon materials in a range of solvents including water, ethanol and tetrahydrofuran. For systems that are easily modified by the process of removing the dispersing medium, it is widely recognised that traditional processes for measuring the specific surface area of the system are unable to offer robust analyses. Simply, the act of drying down the sample for analysis by a technique such as BET can lead to a significant loss of surface area in the system as particles aggregate or coalesce; the resulting adsorption measurement is quite unrepresentative of the original dispersion. In contrast, the NMR technique relies on the presence of solvent and is sensitive to the specific interactions between the solvent and the particle at the interface. The speed of analysis and being able to use concentrated, wet and opaque samples offer significant advantages.

The application of the solvent relaxation NMR will be illustrated through several short case studies using samples including nano carbon blacks, graphene oxide, nanographites, porous graphenes and zinc oxide/graphene oxide composites. The ability to work in a variety of different solvents will also be demonstrated.

The technique is shown to give a good measure of surface area, correlating well with conventional surface area estimates obtained by nitrogen adsorption, TEM or light scattering for the non-porous samples. For samples that are porous, two distinct surface areas can be estimated assuming the two environments ('inner' and 'outer') have the same surface chemistry and that there is a slow exchange of solvent molecules between them. Further, we show that differences in wettability and dispersability between samples dispersed in water, ethanol and cyclopentanone can be observed, along with changes to the surface chemistry of the interface.

Finally, complexes between zinc oxide and graphene oxide will be used to show how a quite complicated sample can be robustly analysed by NMR where BET was unable to provide any useful data at all.

OC028

Microwave assisted purification of detonation nanodiamond and stabilisation of its suspension

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The purity of nanodiamond (ND) is of great importance for the characterization of the properties of ND. Unfortunately, there is a lack of the information on presence of elemental impurities in ND, which was connected for many years with the absence of the sensitive and robust methods for the analysis of this type of nanocarbon material. Recently, a novel simple, rapid, sensitive and accurate method for the determination of metal impurities in detonation ND, based upon the direct injection of aqueous suspensions of nanodiamond into a sector field inductively coupled plasma mass spectrometer (ICP-MS) was developed. This method of direct analysis was capable of the quantification of 55 elemental impurities at concentration levels of 10^{-8} wt. %, with acceptable levels of precision and accuracy for 30 of them, from an aqueous suspension of just 0.1 mg mL^{-1} DND. The further application of ICP-MS method to the analysis of more than 20 commercial samples allowed identification of possible sources for the contamination of various DND samples during their processing.

The careful analysis of the reasons for the contamination and elimination of them caused a significant improvement in the existing technology of their purification. The digestion of amorphous carbon and removal of metal impurities was achieved by treatment with mixture of strong oxidative agents under acidic conditions using microwave oven. As a results the purity of 99.95 mass % was obtained for under optimised for DND.

The stability of DND suspension was investigated with measurement of dzeta potential as a function of pH and aggregate size for different samples. The possibility of the fractionation of DND aggregates on size by using capillary zone electrophoresis was considered. The additional study on modification of dzeta potential of DND was performed.

This work was supported by grants from the Australian Research Council to ACROSS (DP110102046) and CSL (LE0989539).

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In-situ Observation of Meniscus Behavior during Stripe Pattern Formation in Convective Self-Assembly

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Convective self-assembly provides one with simple, scalable, and economical routes to the fabrication of patterned structures of colloidal particles. In our previous studies, we successfully fabricated striped structures (Fig.1)¹ and cluster arrays² with well-ordered periodicity of the order of micrometers in their structure by utilizing the vertical deposition convective self-assembly. Furthermore, conducting the stripe formation after rotating the substrate with the stripes by 90°, we obtained grid network patterns of colloidal particles.³ However, the stripe formation mechanism has not yet been clarified. In the present study, we directly observe the meniscus motion during the stripe formation process in the convective self-assembly of colloidal particles to reveal the formation mechanism.

A hydrophilic substrate was vertically immersed in a suspension and kept stationary at a constant temperature. As the solvent evaporates, dispersed particles are carried into the meniscus tip by the solvent convection, and deposited on the substrate to form stripe patterned colloidal arrays. We captured the meniscus shape evolution with an optical interferometry by illuminating a monochromatic light with the wavelength of $\lambda = 475 \pm 15$ nm at the meniscus tip (Fig. 2). The light reflected on the meniscus and substrate surfaces interferes with each other, resulting in the interference fringe pattern near the meniscus tip. We calculated the thickness profile of the meniscus from the fringe patterns, and clarified the stripe formation mechanism as follows. Under a fairly low particle concentration condition, the meniscus is gradually stretched downward to be concave toward a substrate as the solvent evaporation progresses, because the rate of particulate film growth is slower than that of the liquid level drop due to the solvent evaporation. The convective flow toward the meniscus tip accelerates the deformation of the meniscus, resulting in the rupture of liquid film at the thinnest point of the meniscus. The rupture propagates in lateral directions, and then the meniscus tip slides off from the particulate line and sticks to a new position determined by the equilibrium contact angle.

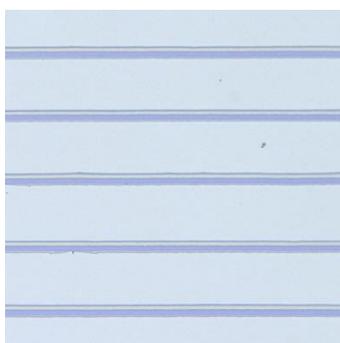


Fig. 1 Stripe pattern

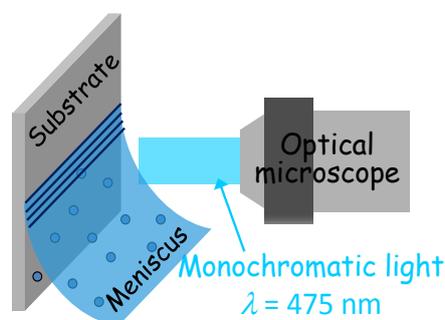


Fig. 2 A schematic of the experiment

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OC030

Specific metal ion triggered phase transition of peplipid-based lipid liquid crystalline dispersion

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A specific metal ion-responsive lipid liquid crystalline (LLC) dispersion system was fabricated, which can work in buffer solutions. The LLC matrix was prepared from phytantriol which spontaneously forms the reversed bicontinuous cubic phase in water,¹ and a novel peptide-lipid conjugate (peplipid) consists of myristate alkyl chain for anchoring into the phytantriol-based cubic bilayer and a peptide sequence for capturing specific metal ion.² The peplipid at its unbound state, when added into the phytantriol-based cubic system induces a positive effect on the bilayer curvature, resulting in the formation of the lamellar phase (vesicles) and the dispersion was transparent in appearance.³ Upon binding of the cadmium ion, the peplipid induces a negative effect on the lipid bilayer curvature and consequently leading to the formation of cubic phase and opaque appearance. In contrast, other metal ions, including buffering salts, could not sufficiently trigger the phase transition due to weak interaction with the peplipid.² The high selectivity of metal ion interaction and triggered phase transition provide potential applications, such as in colloidal-mineral separation,³ triggered drug release⁴ and treatment of cadmium (II) pollution.⁵

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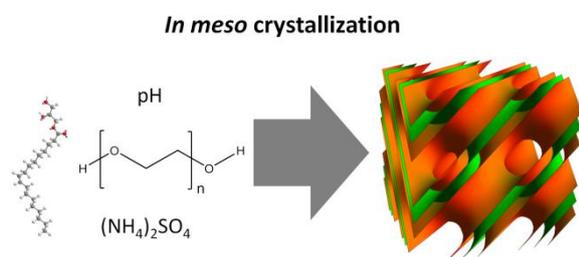
***In Meso* Crystallization: Compatibility of Different Lipid Bicontinuous Cubic Mesophases with the Cubic Crystallization Screen in Aqueous Solution.**

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A novel *in meso* crystallization method has facilitated the structural determination of several biologically relevant integral membrane proteins (IMPs).[1] However, the method remains poorly understood as IMPs are difficult to express and handle. Analogous to solution based crystallization, *in meso* crystallization requires extensive screening of precipitant conditions.[2] Bicontinuous cubic phases are the most commonly used lipid phases for *in meso* crystallization. The effect of the IMPs on the cubic phase and the compatibility of the crystallization screen used with the cubic phase is important; if the underlying 3-D cubic nanostructure is destroyed, the screen or protein and lipid combination may not be suitable for *in meso* crystallization experiments.

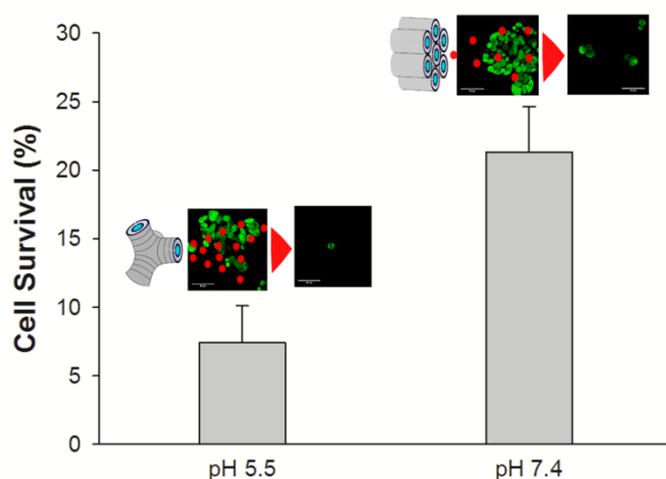
We looked at the impact of a screen specifically marketed as compatible with the cubic mesophase, the Cubic crystallization screen (Emerald Biosystems), on the cubic mesophases formed by three different lipids: monoolein, monopalmitolein and phytantriol. The Cubic screen was found to be compatible with cubic mesophase retention under most crystallization conditions for all three lipids studied. The effect of the individual components comprising the multicomponent screen was deconvoluted in two ways. Initially, the effect of specific poly(ethylene glycol) (PEG) and salt components on the cubic mesophase was determined using high-throughput synchrotron Small-Angle X-ray Scattering (SAXS). The effect of high-molecular-weight (M_w) PEG was shown to dominate the phase behavior within the screen. The effect of additional salts present within the screen becomes important for low M_w PEG molecules. Finally, a recently developed multiple linear regression modeling method was shown to deconvolute the effect of individual components within the screen effectively.[3]



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pH-responsive Lyotropic Liquid Crystals for Cancer TherapyRenata Negrini¹, Wye-Khay Fong^{1,2}, Ben J Boyd², Raffaele Mezzenga¹¹ETH Zürich, Zürich, SWITZERLAND, Switzerland, ²Monash University, Victoria, Australia

Cancer cells are typically characterized by a pH significantly lower than physiological conditions, which paves the way to possible cancer therapies exploiting pH as a trigger. A pH responsive Lyotropic Liquid Crystal (LLC) matrix is developed in this work suiting ideally pH-responsive controlled drug release for tumour treatment. To this end, a weak base, Pyridin-4-ylmethyl linoleate (PML), was synthesized and combined with a neutral lipid monolinolein (MLO), in order to obtain lipid mesophases exhibiting a change in symmetry when PML is protonated in response to pH changes around its pKa (≈ 5.5). The system was optimized by testing different amounts of PML and following the structure evolution at different pH by small angle X-ray scattering (SAXS). The final design composition yielded a bicontinuous cubic phase (Pn3m symmetry) at pH5.5 and a reversed hexagonal columnar phase (H2) at pH 7.4. By exploiting the different intrinsic transport rates of Pn3m and H2, diffusion studies at two different pHs simulating physiological and cancer conditions were conducted by employing glucose and doxorubicin (DOX) as model drugs. Both molecules were shown to diffuse significantly faster (glucose: $DP_{Pn3m} / DH_2 \approx 16$; DOX: $DP_{Pn3m} / DH_2 \approx 45$), in the Pn3m phase at acidic conditions. In vitro drug release studies of DOX conducted at pH 7.4 and 5.5 from the above-designed bulk mesophases coexisting in excess buffer with cancer cell cultures confirmed the potential of the system in cancer therapy, by yielding a three-fold increase in the efficiency by which cancer cells are killed at pH 5.5 versus the physiological pH 7.4. This work provides the first example of a responsive lipid mesophase system in which a spontaneous change in symmetry at pHs characteristic of tumour growth, enhances the release of anticancer molecules, standing as a new drug delivery system for cancer therapy, in which the lower extracellular pH typical of tumour cells - compared to the contiguous tissues and blood- is the only endogenous triggering stimulus.

OC033

Novel Polymer-Coated Lipid-based Liquid Crystalline Nanoparticles for Drug Delivery Applications

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Background and aim: Lipid-based nanoparticles, such as cubosomes and hexosomes have complex internal nanostructures, enabling them to encapsulate high amount of molecules with diverse size and hydrophobicities. Recent studies highlighted the lipid-based nanoparticles have several critical drawbacks that present significant hurdles for their advancement as potential drug delivery agents. These include: a) lack of controlled release for low molecular weight species [1]; b) destabilisation of the nanoparticles due to interaction with intrinsic components in plasma and gastrointestinal tract upon administration [2]; and c) long term chemical and colloidal stability issues. This project aims to create drug delivery nanoparticles with lipid-based cubosome core and bio-degradable polymer coating. The nanostructured core protect and encapsulate actives and the polymer coating provides potential physical barrier to prevent destructive interaction and impart controlled release, as well as the potential for surface functionalization for targeted drug delivery.

Method: Cubosomes composed of monoolein and a surfactant such as negatively charged AOT or positively charged DDAB were mixed with opposite charged polymers such as chitosan (+ve) or pectin (-ve) to induce coating via electrostatic interaction. The structural properties of the particles were monitored using small angle x-ray scattering, micro-electrophoresis and dynamic light scattering. Simulated in-vitro digestion was used to investigate the integrity of the polymer coating in preventing enzymatic degradation of the lipid-based core.

Results and conclusion: The coated particles retained the cubic internal structure and showed polymer dependent size and surface charge variation, indicating effective polymer coating of the cubosomes with minimal impact on the internal core structure. The coated particles also showed significantly lower rate of enzymatic degradation in the simulated digestion study compared to uncoated particles, suggesting high integrity of the polymer coating.

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OC034

Milk goes Nano: Evolutionary Bioengineering in the Human Digestive Tract

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The digestion of dietary triglyceride oils into the amphiphilic products fatty acid and monoglyceride plays a vital role in the delivery of the lipid-soluble bioactive molecules such as hydrophobic vitamins, carotenoids and drugs to the circulatory system of the body. These components have been found to self-assemble into a variety of thermodynamical equilibrium structures under biologically relevant conditions of the human intestine.^{1,2}

Here, the discovery of highly ordered geometric nanostructures during the digestion of model lipids and milk will be discussed: Transitions from normal emulsion through a variety of differently ordered thermodynamically stable nanostructures were observed using time-resolved small angle X-ray- and neutron scattering, and visualized by cryogenic transmission electron microscopy.³ The response of these thermodynamical equilibrium structures to changes in the pH and composition, as well as the location of components within the self-assembled structures, will be presented.⁴

The results will help to understand the process of lipid digestion with a focus on colloidal structure formation and transformation for the delivery of hydrophobic functional molecules and may indicate a compensating mechanism for the maintenance of lipid absorption under compromised lipolysis conditions.

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Amyloid Fibril Morphology: Relevance to Disease and Biomaterials

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Amyloid fibrils are implicated in over 20 degenerative diseases. The mechanisms of fibril structuring and formation are not only of medical and biological importance but are also relevant for material science and nanotechnologies due to the unique structural and physical properties of amyloids.¹⁻² We found that hen egg white lysozyme (HEWL), homologous to the disease-related human lysozyme, can form left-handed giant amyloid ribbons, closing into nanotubes.³ Networks of HEWL fibrils adsorbed to solid supports were also able to promote the physiological adsorption and spreading of a range of eukaryotic cells.¹ In order to obtain an improved fundamental understanding of the molecular processes that underpin fibril assembly we used a combination of nanoscale analytical techniques to follow the assembly of a peptide based amyloid fibril at length scales from the molecular to the micron.⁴ These results will improve our understanding of structure-function relationships of amyloids in relation to neurodegenerative disease and materials science.

By using matrix-assisted laser desorption ionization mass spectrometry analysis, we identified a short peptide sequence, which drives amyloid formation in HEWL, namely the ILQINS hexapeptide. By combining atomic force microscopy and circular dichroism, we found that this fragment, synthesized by solid phase peptide synthesis, also forms fibrillar structures. However, all fibrillar structures formed possessed an unexpected right-handed twist, a rare chirality within the corpus of amyloid experimental observations. We confirm by synchrotron based small- and wide-angle X-ray scattering (SAXS/WAXS) and molecular dynamics (MD) simulations that these fibrils are composed of conventional left-handed β -sheets, but that packing stresses between adjacent sheets created this unusual chirality. We also show that the right-handed fibrils represent a metastable state present before the formation of β -sheet-based microcrystals.

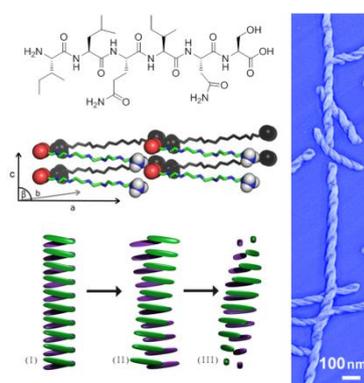


Figure 1: ILQINS readily forms fibrils (right), modeled by MD (bottom left) based on WAXS spectra

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OC036

Employing QCM-D to Characterise Fibronectin and Bovine Serum Albumin Adsorption and Conformational Dynamics on Inherently Conducting Polymers

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Inherently conducting polymers (ICPs) such as pyrrole (PPy) and poly(3,4-ethylenedioxythiophene) (PEDOT) are currently the subject of intense research in the fields of biomaterials and bioelectronics. They possess inherent biocompatibility, as well as the ability to perform a range of biologically relevant functions, including the controlled delivery of drugs and growth factors, as well as mechanical and electrical stimulation. Due to their highly tuneable physicochemical and electrochemical properties, a range of approaches and techniques are being employed to both understand, and control, the nature of biomolecular and cellular interactions with the ICP nanostructured materials. These include modulating the concentration of the dopant species during polymerisation, as well as the incorporation of biological, rather than synthetic, compounds as the dopant that is aimed at enhancing polymer biocompatibility and biofunctionality.

Critical to the biointerfacing of all biomaterials is the nature of the initial proteinaceous conditioning film that adsorbs to the biomaterial surface upon introduction into an in-vitro or in-vivo environment. The recruitment, retention and conformational structure of proteins on a biomaterial are vital to promoting either favourable or adverse cellular and tissue responses. Herein we present a quartz crystal microbalance (QCM) study of the adsorption and conformational dynamics of the model protein bovine serum albumin (BSA) and the extracellular matrix protein fibronectin (FN) to PPy biomaterials doped with the bioactive dopant dextran sulphate (DS). QCM with dissipation monitoring (QCM-D) is a highly sensitive surface sensing technique that allows both the mass and mechanical properties of the surface bound layers to be determined. Protein adsorption was characterised as a function of DS loading in the polymeric films and surface nanoroughness. The ability for QCM-D to measure the nature of protein interactions with the polymer surface in real-time allowed dynamic adsorption processes to be resolved. Furthermore, we investigated the influence of electrical stimulation on the adsorption of the proteins to the ICP films, illustrating the polymer redox state to significantly modulate protein binding with the material surface.

AFM for Immunohaematology Applications

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The Atomic Force Microscopy (AFM) is becoming a popular tool for biological imaging as it requires minimal pre-treatment to samples, and more importantly, has the ability to image samples in physiological conditions for biological matters and characterize the forces involved [1]. Multiple AFM studies have been done on red blood cells (RBCs). However, the effect of the interaction between blood group antibodies and antigens on the RBC has not been extensively studied and is poorly understood. In this study, we first investigated how AFM can quantify the structure and mechanical properties changes of the RBC triggered by the environment. Second, we measured the affinity forces involved in agglutination.

The blood group antigens may be proteins, glycoproteins or glycolipids integrated in the red cell membrane [2]. We generated a hypothesis that the membrane structure will be altered, leading to a change in the morphology of the RBC upon interaction between blood group antigens and blood group antibodies. Dried blood film of RBCs without antibody treatment and RBCs treated with specific/non-specific blood group antibodies were prepared. Images of RBCs were obtained using the tapping mode on the AFM. Changes of RBC morphology were recorded after the RBCs were treated with antibodies, regardless of specificity of antibodies. Multiple factors including the ionic strength of antibody solution, incubation temperature and pH can contribute to the morphology change. The presentation will highlight how the environment affects RBC shape and mechanical properties.

AFM in force mode was also used in conjunction with non-functionalized and functionalized cantilever tips to characterize RBC membrane properties and quantify antibody-RBC antigen interactions respectively.

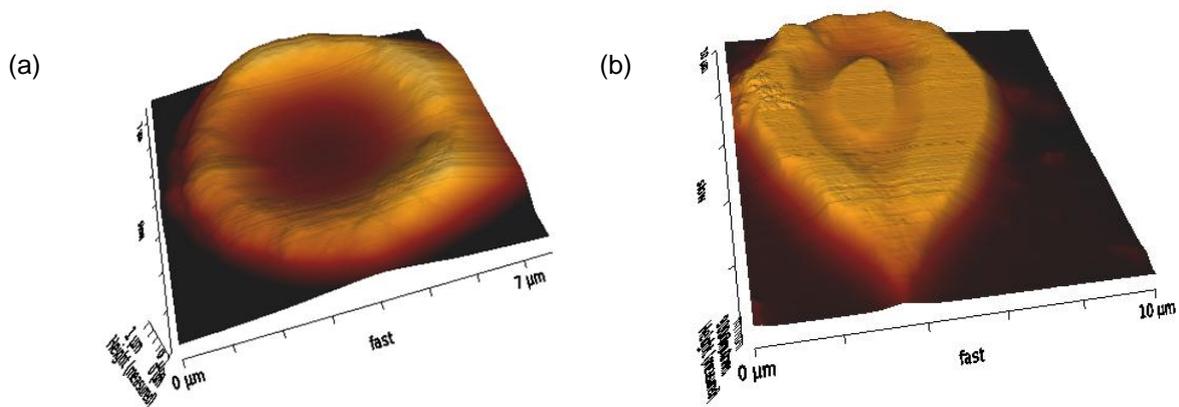


Figure 1. (a) Positive red cell without incubation with specific antibodies. (b) Positive red cell after incubation with specific antibodies at 37°C for 30 minutes.

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OC038

“Watching” Single Proteins in Action on Material Surfaces using High-Speed Atomic Force Microscopy

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We are currently undertaking research on protein- and cell-material interfaces, particularly the understanding of nanoscale and molecular interactions for enabling cell growth, development and repair. In this research, the use of conventional approaches for studying the dynamics of molecular interactions with materials and surfaces is challenging. For example, the often rough, opaque and fluorescent quenching properties of real-world materials such as polymers or ceramics are not amenable to optical and fluorescence techniques for tracking single molecule dynamics. This is where some of the emerging nanoscale and molecular characterization techniques, such as High-Speed Atomic Force Microscopy, present exciting opportunities for revealing the molecular-level dynamics on material surfaces.

This presentation will highlight research on the use of High-Speed Atomic Force Microscopy (HS-AFM), which massively surpasses the capabilities of conventional AFM systems by enabling acquisition times of 50-100 milliseconds per image (10 - 20 frames/second). This takes AFM into the realm of video rate imaging that is defined as achieving speeds of ≈ 12 frames/sec; the human eye needs to visualize a sequence of images at this speed in order to perceive motion. Coupled with the ability to achieve 1-2 nanometer lateral image resolution in liquid, the HS-AFM has the unique ability to provide significant insight into both the nanoscale structural and interaction dynamics of single molecules and molecular assembly processes on surfaces in real-time.

We will show results on the dynamics of single fibronectin proteins on mica, gold and polymer substrates with temporal resolution ranging from 2 – 10 frames/sec (i.e. 2 – 10 AFM images per second) (see Figure 1). The sequence of AFM images, which effectively produce a movie clip, reveal the single proteins as they, diffuse, rotate and interact with neighbouring proteins on the surface. After visualizing the dynamics of single protein – surface interactions, we also observe the two-state adsorption processes, including protein saturation and formation of a protein layer.

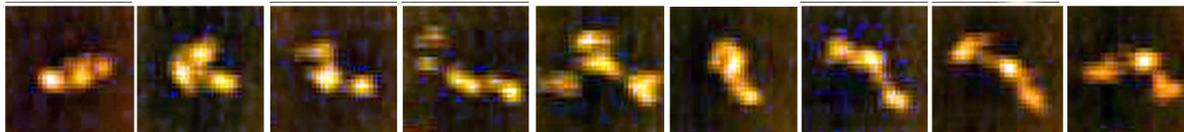


Figure 1. Fluctuation dynamics of semi-unfolded single fibronectin protein on a material surface in liquid. Protein size = ≈ 40 nm. Imaging time starting from left image is 250 milliseconds per image.

Structure and Dynamics at the Nano-Bio Interface: Insights from Molecular Simulations

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Biomolecules adsorb differently to nano-structured materials and this phenomenon is being now widely exploited for engineering novel materials and devices for biomedical applications. At the same time, there is little knowledge about how engineered nanomaterials can interfere with the overall biological molecular machinery [1]. Theoretical modelling can help get insights into the molecular mechanisms of biomolecular interactions of nanomaterials which can be exploited to improve molecular recognition needed for safe and efficient biomedical applications. However, some serious challenges exist in developing an adequate approach to modelling nano-bio systems with rigor and efficiency [2]. Therefore, when applying molecular simulations to nan-bio systems it is essential to design a molecular model and select simulation approaches that will provide physical insights into the phenomena of interest while also addressing the limitations. In this talk examples of our recent simulations performed in conjunction with experimental studies will be presented. These include: (1) effects of nano-structuring on protein adsorption to nanoparticle surfaces [3, 4]; (2) effects of peptide density on the efficiency of functionalised nanoparticles for membrane internalisation [5]; (3) effects of structure and dynamics of the functional peptide layer on the efficiency of epitope conjugated Au nanoparticles for biosensing [6].

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Inexpensive Surfactants with Low Fluorine Content Exhibiting High Water-Solubilizing Power in Low Pressure Supercritical CO₂

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Supercritical CO₂ (scCO₂) exhibits n-hexane-like polarity along with the nontoxic, non-flammable and inexpensive properties. This has led to its acceptance as a green solvent for environmentally friendly and energy-saving technologies. However, the poor solubility of polar solutes means there are only limited industrial applications of scCO₂. This study explores effective and efficient fluorocarbon (FC)-tail structures able to form water-in-scCO₂ microemulsions (W/CO₂ μEs) and hence improve polar molecule solubility in scCO₂. To improve environmental compatibility, these surfactants have been designed to have only limited fluorine content (number of fluorine atoms per molecule, $N_F \leq 27$).

The surfactants studied here are 3FHT(MO)₃, 3FT(EO)₃ and 4FT(EO)₃ which have the structure R_FOCOCH₂-CH(-COOR_F)-CH(-COOR_F)-SO₃Na, where R_F (the fluorocarbon tail) is CF₃CFHCF₂CH₂-, F(CF₂)₃CH₂CH₂- and F(CF₂)₄CH₂CH₂- respectively. As control surfactants, two double-FC-tail surfactants, 4FG(EO)₂ and 6FG(EO)₂ with the structure R_FOCOCH₂-CH₂-CH(-COOR_F)-SO₃Na, where R_F is F(CF₂)₄CH₂CH₂- and F(CF₂)₆CH₂CH₂- respectively were also studied to confirm the effect of tail number on the solubility and solubilizing power. To investigate the basic interfacial properties (Critical micelle concentration (CMC), surface tension and occupied area per molecule at the CMC), aqueous surface tensiometry was performed at atmospheric pressure and 35°C. CMC values were 2.8×10^{-6} M for 4FT(EO)₃ ($N_F=27$), 8.4×10^{-5} M for 3FT(EO)₃ ($N_F=21$), and 2.5×10^{-4} M for 3FHT(EO)₃ ($N_F=18$), clearly showing that the decrease in the number of fluorine atoms per surfactant molecule (N_F) causes an increase in the CMC by lowering the FC-tail hydrophobicity. The N_F value also affected surface tension at the CMC with values of 18.3 mN/m at $N_F=27$ increasing to 19.0 mN/m at $N_F=21$ with further increases to 20.0 mN/m at $N_F=18$. However, the low surface tensions (≤ 20 mN/m) obtainable even for short FC-tails with low N_F suggests that W/CO₂ interfacial tension will be very low facilitating the formation of W/CO₂ μEs.

Surfactant solubility in scCO₂ was examined by visual observation of 17 mM surfactant/W/CO₂ mixtures. It was shown that above certain pressures all surfactants yielded transparent single-phases identified as W/CO₂ μEs. Decreasing pressure caused a turbid phase to form, representing pressure (or CO₂ density) induced phase transition from microemulsions to macroemulsions. At water-to-surfactant molar ratio (W_0) = 18, the phase transition pressures of all triple-tail surfactants were lower by ~40 bar than those of double-tail surfactants, even when N_F values were comparable (i.e. 4FT(EO)₃ vs 6FG(EO)₂ ($N_F=26$) and 3FHT(EO)₃ vs 4FG(EO)₂ ($N_F=18$)).

UV-visible absorbance of aqueous methyl orange (MO) solution solubilized in 17mM surfactant/CO₂ mixtures was measured as a function of W_0 to examine the solubilizing powers of each surfactant. In stable μEs, the addition of MO solution (and hence increasing W_0) gradually increases the UV absorbance until the maximum W_0 the surfactant can solubilize is reached (W_0 70 is the case of 17mM 3FHT(EO)₂ at 45 °C and 350 bar). 3FHT(MO)₃ was found to solubilize water in CO₂ as much as the larger N_F surfactants 3FT(EO)₃ and 4FT(EO)₃ which, due to less expensive FC-tail (25gs of R_FOH cost AU\$70 for 3FHT(EO)₃ and AU\$180 for 4FT(EO)₃ or 4FG(EO)₂), demonstrates the highest cost-performance as a solubilizer for W/CO₂ μEs.

OC041

Drag Reduction in Water by Leidenfrost Vapour Layers Sustained on Superhydrophobic Surfaces

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One innovative approach to achieve drag reduction on a solid body moving in liquid is to introduce a lubricating gas layer between the body surface and the surrounding liquid. We demonstrate and quantify a highly effective hydrodynamic drag reduction technique that exploits the Leidenfrost effect to create continuous and robust lubricating vapor layer on the surface of a heated solid sphere moving in a liquid. When a perfluorinated liquid with low boiling point is used we show that such vapor layers can reduce the hydrodynamic drag by over 85%¹. These results appear to approach the ultimate limit of drag reduction possible by different methods based on gas-layer lubrication. To extend this approach to aqueous medium we use a nanoparticle coating to make a steel sphere surface superhydrophobic resulting in a reduced initiation temperature, and enhanced dynamic stability of the vapor layer². The vapor layer induces a gradual reduction of the drag coefficient on heated spheres freely falling in water³. In addition to the drag reduction we found that such vapor layer can also stabilize the sphere fall trajectory. The drag reduction is shown to operate in the Reynolds number range that spans the drag crisis in the absence of the vapor layer. The drag reduction and drag crisis moderation are attributed to the disruption of the viscous boundary layer by the vapor layer³. The results of this study are expected to stimulate the ongoing efforts to develop effective and unexpansive drag reduction technologies based on the sustainability of vapor layer on textured superhydrophobic surfaces.

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Sweetness and light: an exploration of novel sugar photosurfactants

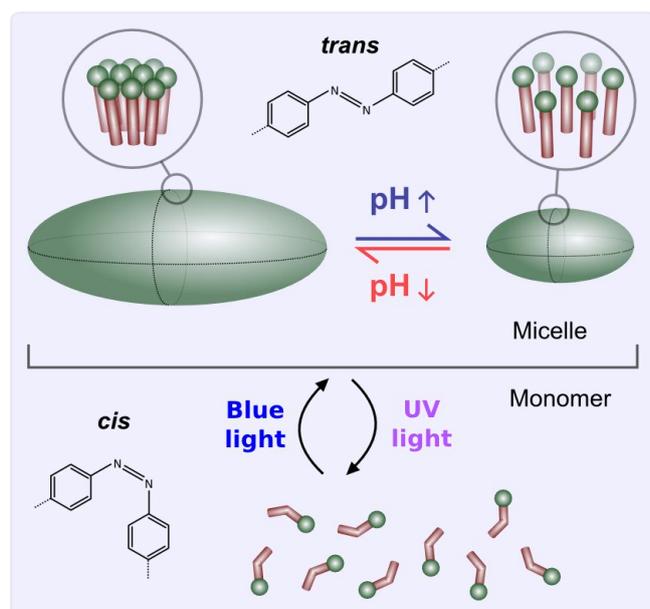
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A library of novel photo-switchable sugar surfactants have been synthesized by coupling a butylazobenzene tail group to a head group comprising tri(ethylene glycol) and a sugar with or without a triazole linker [1]. Despite their relative molecular simplicity and the robust synthetic steps required, these molecules exhibit a remarkable range of desirable properties, including widely varying micelle morphologies, photo-control of surface tension, and - through oxidation of the sugar to a uronic acid - pH control of aggregation and surface properties.

As expected from the azobenzene chromophore, rich liquid crystal phase behaviour is noted in a range of solvents. We characterise these surfactants using spectroscopy, tensiometry and small-angle neutron scattering (SANS), and demonstrate that their multiple functionalities provide opportunities for sensitive control over the properties of colloidal and soft matter systems. Scattering measurements demonstrate that both light and pH can be used to control micelle morphology and aggregation number.

These materials uniquely combine the desirable characteristics of both sugar surfactants (water solubility, biological activity and specificity, wide ranging aggregation geometry) and azobenzenes (photo control of interfacial and aggregation properties and rich liquid crystal phase behaviour).



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OC043

Sticky, floppy bilayers and the resulting mess.

Stephen Hyde

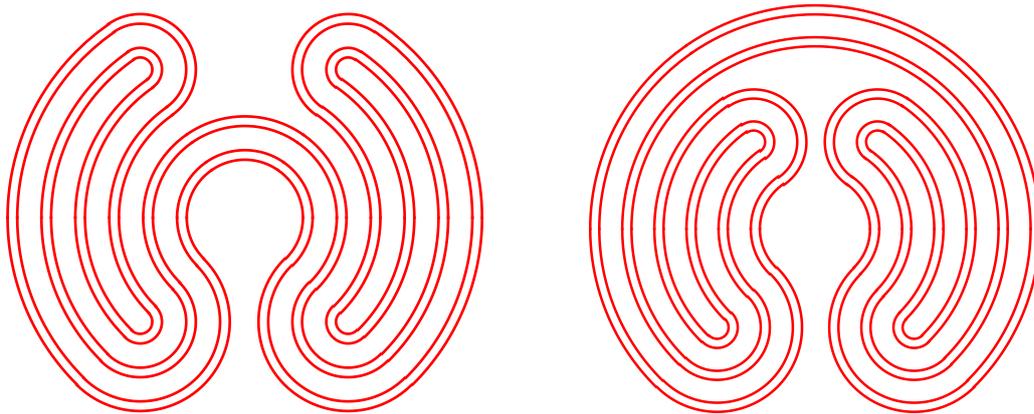
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A curious feature of bicontinuous cubic membrane morphologies *in vivo* that distinguishes them from synthetic bicontinuous cubic phases *in vitro* is that the highly swollen biological examples often contain multi-lamellar stacks, folded in parallel.

A simple analogy is single bilayer vesicles vs. multi-bilayer examples.

One route to the formation of these multilayer patterns is via proteins that favour transient attractions between apposed bilayers via the intervening cytosol [1]. We can naïvely model that effect via “sticky bilayers”, where the glue corresponds to proteins embedded in the bilayer and known to condense bilayers *in vivo*. A zoo of topologically accessible “folded” patterns are possible.

I have developed a simple “algebra” that describes that zoo for the simplest starting shape, namely a spherical bilayer vesicle. (The simplest species in that zoo has also been identified recently in simulations of transitions in “soft shells” [2].) Various species can then be ranked by their bending energies. We can balance that energy by the resulting sticky bilayer overlap, resulting in a simple, undoubtedly idealised, model of these multi-bilayer stacks. A spectrum of shapes result, containing (In general) $4z$ stacks, where z is any positive integer. Two examples of patterns ($z=3$) are shown below, where each red arc describes an individual bilayer. Both shapes can be inflated to give single-walled spheres.



This schema can be extended to other starting topologies, including sponge-like configurations. The model leads to explanations of some of the complex and curious patterns seen in EM images over the past decades (see, e.g. [1]).

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Nanostructures at Oppositely Charged Surfactant – Polymer Interfaces

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Oppositely charged surfactant and polymer complexes are of increasing interest as they offer great versatility in structure manipulation for use in various applications in the food, cosmetic and pharmaceutical industries. Over the past four decades, factors influencing the electrostatic and/or hydrophobic interactions between these charged species and their equilibrium phase behaviour have been well studied. These parameters include the surfactant-to-polymer molar ratio, surfactant chain length, polymer molecular weight and charge density, temperature, additives, pH and salt concentration. However, little research has been conducted to investigate the dynamics of liquid crystalline nanostructure formation at the interface between these materials.

A novel approach was developed to understand the growth and development of highly ordered structures at such interfaces and how the chemical composition changes over time. Crossed-polarising light microscopy (CPLM) allows visualisation of phases exhibiting birefringence. Whilst more elaborate structural and compositional data can be spatially resolved by rastering across the interface with synchrotron small angle X-ray scattering (SAXS) and Raman microscopy, respectively.

The industrially relevant system studied comprised of poly(diallyldimethylammonium chloride) (polyDADMAC) and sodium dodecyl sulphate (SDS). Results demonstrated the appearance of hexagonal phases possessing different internal dimensions with co-existing micellar phase in particular regions at the interface. The rate of structure formation was controlled by diffusion of the oppositely charged molecules across the interface, which can be impeded by the liquid crystalline structure already present at the interface. In addition, the direction of structure growth was influenced by the degree of mobility each solution holds and the ability of the charged species to traverse the highly ordered structure(s) that may locally exist at equilibrium.

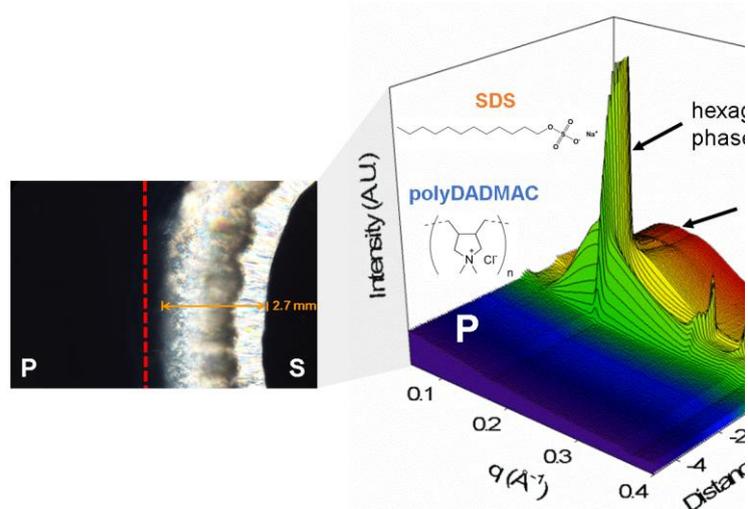


Figure 1. CPLM image and SAXS profile at the polymer(P) – surfactant(S) interface.

Liquid crystalline phases are excellent candidates as drug delivery systems as they have the ability to solubilise various therapeutics with a diversity of physicochemical properties. It is well known that the nanostructure dictates the rate of drug release from these matrices, therefore having control over which mesophase is formed would be advantageous. The outcomes from these studies will be significant in understanding how such systems may be tuned to provide a novel and interesting route to tailored release nanomaterials.

OC045

Cubosomes and Cubic Phase Interfacial Dynamics

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³*Monash University, Melbourne, VIC, Australia*

Self-assembly of lipids and other amphiphiles produces a wide array of structures with complex equilibrium phase behaviour. Of these, bicontinuous and hexagonal phases are of particular interest because their rheology is uniquely able to resist flow. In spite of their highly elastic state, their molecular mobility remains quite high and allows them to rapidly exchange materials via diffusion. The kinetics of diffusion into cubic phases can affect relevant variables like particle shape, surface interactions, and release of solubilized materials. We use microscopic observations of diffusion into, and out of, cubic and hexagonal phases to relate the rate of phase growth and response to different chemical and biological mechanisms for inducing structural changes. Microrheological studies of cubic-solvent interfaces are used to enhance understanding of non-equilibrium structural transitions that influence cubic phase stability and applications as colloidal templates.

OC046

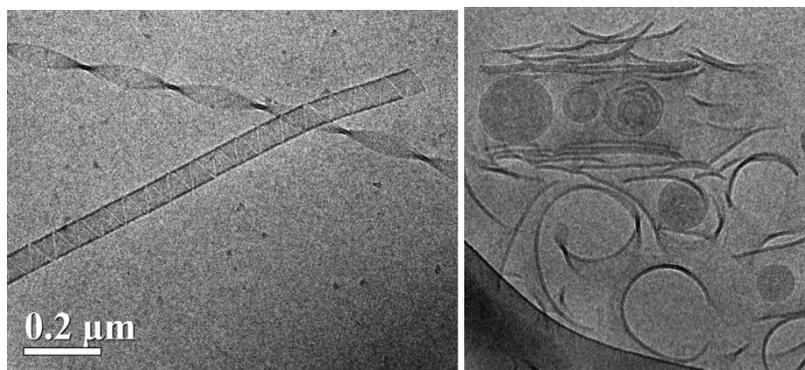
1D Self-assembly of Phospholipids into Micro- and Nano Tubular Structures

Luba Kolik, Irina Portnaya, Dganit Danino

Technion - Israel Institute of Technology, Haifa, Israel

Natural as well as synthetic amphiphiles, including proteins, peptides and lipid systems form 1-dimensional (1-D) structures as ribbons and tubules. The study of this aggregation into micro- and nanostructures is of great importance for both basic research and for technological applications [1].

Yager and Schoen [2] were the first to observe tubules in dispersions of 1,2-bis(tricosyl-10,12-diyndyl)-sn-glycero-3-phosphocholine, designated DC_{8,9}PC. Addition of short chain alcohols, or mixing with short-chain PC lipids was found to have a profound influence on the bilayer structure and aggregates morphology [3]. Here we report on cryo-transmission electron microscopy (cryo-TEM) and calorimetry analysis applied to define the balance of forces and interactions that dictate the equilibrium structures and their properties. Combined with recent studies on peptide amphiphiles [4,5] we gain deeper understanding of 1D assembly processes.



1D morphologies in phospholipids solutions: Why and How do they form?

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OC047

Probing molecular interactions at the cell-polymer electrode interface using single cell force spectroscopy

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Cell-material and cell-cell interactions are important in biomedical engineering, tissue engineering and bionics, and critical for our understanding of the functional integrity of living cells. There are several physiological and biological aspects of cell-material and cell-cell interactions such as glycan interactions¹, soluble signaling factors and integrin receptor binding². Many of these interactions, particularly via extracellular matrix constituents, are emulated in synthetic biomaterials to control cellular responses (e.g. proliferation, adhesion and differentiation). To address the complexity of these interactions, “intelligent” biomaterials are often used to enable the dynamic, temporal and spatial control of cell adhesion via chemical, mechanical and electrical stimuli. However, the mechanisms by which these stimuli control cell-material adhesion are not well understood at the nanoscale and molecular level (e.g. single integrin binding). Numerous qualitative and semi-quantitative assays have been utilized to investigate cell adhesion.³ Conventional techniques, like washing assays and hydrodynamic flow assays⁴, are commonly used but do not probe dynamic binding events on different timescales (e.g. initial adhesion), are pseudo-quantitative with no direct measurement of the molecular binding forces, and/or do not reveal cell subpopulations that may result from different functional states of individual cells.

Here, we introduce a technique based on Atomic Force Microscopy (AFM) termed “Single Cell Force Spectroscopy” (SCFS) as a versatile tool for studying cell adhesion on biomaterials. The SCFS is implemented by attaching a live cell on the end of an AFM probe to enable direct measurements of cell adhesion. We are particularly interested in applying the SCFS to measure cell adhesion on inherently conducting polymers (ICP)⁵ within an electrochemical AFM setup to address the challenges of characterizing dynamic properties and nanoscale interactions at electrode-cellular interfaces. Previous studies in our group have demonstrated the ability to control protein and cell adhesion on conducting polymers via electrical stimulation⁶. However, the underlying mechanisms of controlling the cellular response at the single molecular level are poorly understood, particularly as a function of electrical stimulation.⁷ The presentation will highlight exciting possibilities for controlling live cell adhesion with switchable conducting polymers, in addition to providing significant insight on the molecular binding, such as cell receptor–ECM protein binding, which is involved in the interactions. These studies add another dimension to our knowledge of developing next generation conductive biomaterials and use of electrical stimulation for tissue engineering, medical devices and stem cell therapies.

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OC048

Maximizing Transfection Efficiency of Vertically Aligned Silicon Nanowire Arrays

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SUMMARY

Here, we report on the fabrication of vertically aligned silicon nanowire arrays and on their application for the delivery of genes into a diverse range of cells including cell lines and primary cells.

INTRODUCTION

Gene delivery is now a viable strategy for treating a number of diseases and disorders [1]. However, existing strategies for delivering bioactive species into cells (e.g. by physio-chemical means) are limited either by the range of chemical and biological species that can be delivered, by low efficiency of delivery or by high toxicity [2]. In analogy to the way needles are used in macroscopic medicine to transport drugs or diagnostic agents into living tissue, vertically aligned silicon nanowire (VA-SiNW) arrays can be used in micro-scale biological systems to transport biomolecular cargo into mammalian cells [3]. We focus on understanding the influence of the geometrical parameters within the VA-SiNW arrays on the delivery of DNA plasmids into various types of mammalian cells.

This talk will explore the application of VA-SiNWs in gene delivery. I will first give a brief overview of the current strategies for gene delivery including pros and cons. This will be followed by introducing nanostructured silicon-based materials properties, fabrication and characterisation aspects, including the variety of methods for colloidal chemistry lithography. Then, I will explain how VA-SiNW arrays are utilised to efficiently introduce biomolecular cargos to mammalian cells with minimal impact on the cells' viability and function; including examples of recent applications in the field. Finally, I will present the critical geometrical parameters in the design of the free standing ordered VA-SiNW arrays such as: NW density, diameter and length, which are needed to be taken under consideration to maximize cellular transfection efficiency in mammalian cells.

CONCLUSIONS

We investigated the influence of physical parameters of VA-SiNW arrays on the delivery of genetic cargo into various mammalian cells, by varying systematic geometrical parameters (NW aspect ratio and interpillar spacing).

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OC049

Bacterial Patterning at the 3-Phase Line of Microtextured Lipids

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The relationships of surface microstructure to bacterial adhesion represents a growing focus of interfacial research due to its broad impact ranging from biofilm formation to invasive pathogen binding. Both surface composition and topology have recently been employed to inhibit bacterial adhesion through understanding and replicating antifouling surfaces. In particular natural surfaces, such as some insect wings with high aspect ratios, have been shown to provide self-cleaning, superhydrophobic and antibacterial functionalities. It is well known that the microenvironment resulting from spatial confinement of bacteria significantly influence cluster and colony formation and the subsequent diffusion of extracellular molecules and the bacteria cells themselves. In this study, we examine the underlying mechanisms that dictate the interaction and structuring of bacterial microbes on microtextured C_{20} and C_{22} surfaces as analogues to the dragonfly epicuticle, achieved through the templating ability of highly ordered graphite (HOPG) due to its homogeneous surface structure. The introduction of the alkane microcrystal topology to a surface: (a) limited the extent of adhesion of the bacteria overall but, where adhered it produced predictable structures, and (b) prevented attachment of bacteria to the underlying substratum. Both bacteria elegantly patterned as they adhered at the 3-phase line produced by the alkane microcrystallites forming a heterogeneous interface with air-water in the Cassie-Baxter regime.

OC050

Electroactive Polymer Coatings for Antifouling

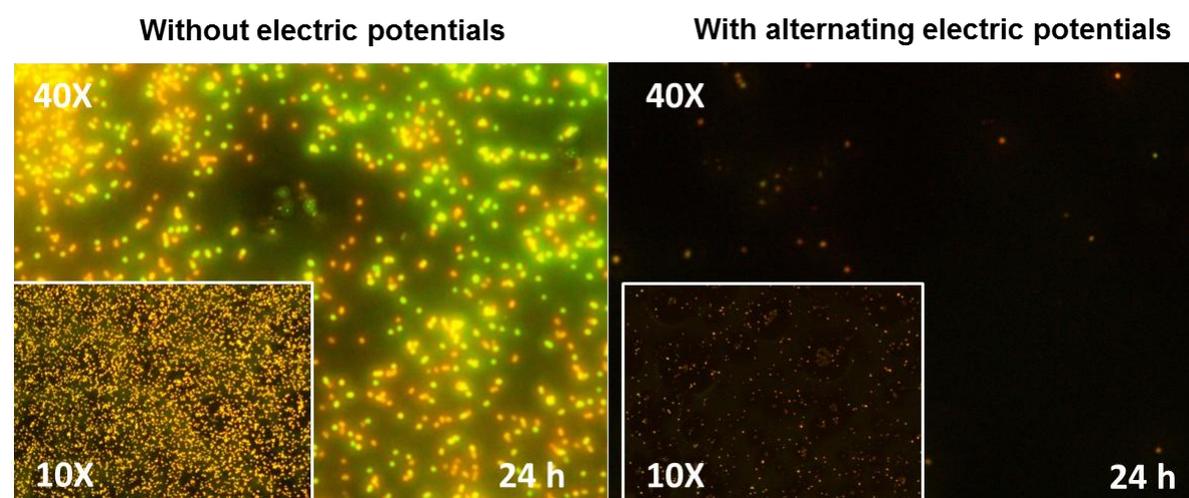
Mikael Larsson¹, Ali Yousefi^{1,2}, Sait Elmas¹, Thomas Nann¹, Magnus Nydén¹

¹University of South Australia, Mawson Lakes, South Australia, Australia, ²Tarbiat Modares University, Tehran, Iran

Marine biofouling is a worldwide problem with significant negative economic and environmental consequences. Traditionally, biofouling was prevented by thick coatings loaded with biocides. However, this era is coming to an end as concerns are raised about the ecotoxic effect of these substances. Biocide-free antifouling alternatives have therefore been intensely researched with a few technologies already on the open market. Unfortunately, these technologies only work for fast moving vessels and not on static vessels or constructions, which are the ones most prone to fouling.

Here we present a novel alternative concept for a biocide-free antifouling coating. It is based on the hypothesis that external energy is required. We have developed a nano-thin coating of polyhydroquinone (PHQ), a polymer that releases and absorbs protons upon oxidation and reduction, respectively. By applying an alternating electric potential of less than 0.5 V (Vs AgCl) a dynamic coating-water interface was enabled, likely through a local variation of pH. It was shown *in vitro* that the coating greatly reduced the fouling by the marine biofilm-forming bacteria *Vibrio alginolyticus*.

The results suggest that standard batteries or solar cells could power the coating, which we believe makes it feasible as a large-scale antifouling technology. Furthermore, since the coating is extremely thin it can be used at the surface of optical sensors, windows and microporous membranes.



OC051

Lifecycle of the Antibacterial Triclosan: Understanding the Partitioning in SDS Systems

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With the rise of liquid soaps, and consumers becoming more environmentally conscious manufacturers have two duties of care; one being to ensure adequate bug inhibition and the other to ensure that an excessive burden is not placed on the environment by any benefit agent [1,2]. Recently there have been concerns about the excessive use of certain benefit agents [3].

It is key to deliver the right amount of Triclosan to the right place at the right time so that at least the Minimum Inhibitory concentration is delivered but not to over deliver which causes waste. The partitioning of the poorly water soluble Triclosan is dependent on pH as well as the concentration of SDS. It is important to understand the partitioning in these soap system to understand factors such as bioavailability and deposition. We propose a model for partitioning between free Triclosan and Triclosan in micelles, and between anionic and neutral forms based on an NMR study.

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OC052

Molecular adsorption dynamics in advanced water treatment: What gets through the treatment process?

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Water treatment to produce potable quality water from a range of sources is a global issue that relies increasingly on the treatment of water from catchments in populace areas. This water may be from a well-protected reservoir or underground aquifer but more frequently, water is from a source with a significant fraction being the effluent from waste water treatment, industrial water treatment and stormwater from urban and peri-urban areas. There are a number of concerns in the treatment of such waters, including the presence of pathogens as well as a large range of residual chemicals of concern (COC's) from human activities including heavy metals, inorganic ions, pharmaceuticals, poly-aromatic hydrocarbons, PCB's, dioxins, pesticides, herbicides and a range of other organic molecules.

In the past year, we have developed an advanced water treatment plant in conjunction with a range of partners to assess, amongst other things, the removal efficiency of chemicals of concern from a waste water feed. The process plant is a 20 kL/day facility with six barriers for pathogen and COC removal. The barriers include ozonation, ceramic microfiltration, biologically activated carbon, reverse osmosis, UV disinfection and chlorination. In excess of 1200 chemical compounds have been assessed (and continue to be assessed) through a variety of analytical and bioassay techniques across each of the barriers as well as characterisation of the feed. The feed, being the effluent of a waste water treatment plant, contains a range of molecules that have not been removed from solution by biological treatment or adsorption, despite ample opportunity.

A key question is whether advanced water treatment including oxidation (ozonation) to induce molecular mineralisation followed by nanofiltration and further biological action and adsorption is an adequate step in removing these COC's. This is an important consideration since bioassay of the feed to the plant shows significant activity on estrogen, androgen, aryl hydrocarbon, thyroid and other nuclear receptors.

The aim of the work is to classify the risks posed by molecules that are able to avoid the advanced water treatment process through a resistance to oxidation, biodegradation, rejection by membranes and adsorption. This risk is being assessed based on the molecular weight, charge and hydrophobicity of the molecule in an environment where there is continuous competition for adsorption sites. This is quite different from many laboratory experimental scenarios where the adsorption area is effectively infinite. An overview of molecules that are deemed to be high risk and their characteristics will be presented.

OC053

Drainage of Vertical Liquid Films at High Electrolyte Concentration

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¹*Ian Wark Research Institute, University of South Australia, Mawson Lakes, SA, Australia,*

²*Phenomix and Bioinformatics Research Centre, University of South Australia, Mawson Lakes, SA, Australia*

Foam stability is of crucial importance in many processes and mineral flotation in particular. Water with higher salinity levels could be used in the flotation process to address environmental concerns and cost considerations. In froth flotation, frothers and collectors are used to optimise the flotation of minerals, but these are surfactants and often contribute to foam stability. The stability of the foam is strongly affected by the behaviour of the thin liquid film between the bubbles and will be influenced by the solution composition including electrolyte at high concentrations. Therefore the behaviour of the thin liquid film between the bubbles and its subsequent drainage, at elevated electrolyte concentrations is highly relevant. This study investigates the drainage of liquid films stabilised by an anionic (SDS), a cationic (CTAB), or a non-ionic (Brij-35) surfactant at elevated salt concentrations. The drainage is followed at surfactant concentrations below, at, and above the CMC. Interferometry is used to observe film thickness evolution during gravity driven drainage. The overall trend is that film lifetime decreased as the salt concentration increased. We will discuss the role of the type of surfactant and its concentration with respect to its CMC and salt concentration on the film stability.

OC054

Modelling Adsorption of Citrate on ZnO Surfaces

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The shape of ZnO single crystals particles grown under hydrothermal conditions can be controlled by the addition of small organic molecules. For example, additions of citrate hinder growth along the c-axis direction resulting in plate-like particles while hexamine encourages growth along the c-axis resulting in rod-like particles. Density Functional Theory (Gaussian 09) modelling has been used to better understand how the citrate anion adsorbs on to ZnO surfaces. First, the model chemistry which best describes the carboxylate anion molecules in solution is determined using a combination of a solvent model (SMD) with and without one or two explicit water molecules. Secondly, the method for prediction of IR spectra (specifically carboxylate stretching modes) is optimised. Finally, predictions of the IR spectra of citrate adsorbed to ZnO c-plane, ZnO nanoclusters and Zn cations in aqueous solution are compared to experimentally measured spectra of citrate adsorbed to ZnO basal plane to gain understanding of the conformation of the molecule at the surface. Based on the positions of the experimentally observed peaks from the stretching modes of the carboxylates, it appears most likely that the citrate anion has two carboxylates and perhaps the hydroxide participating in the bond to the surface. The modelling suggests that this configuration does not exist on a pristine atomically smooth ZnO surface. Instead, binding to a step or island results in the predicted IR spectra that most closely resembles that experimentally measured.

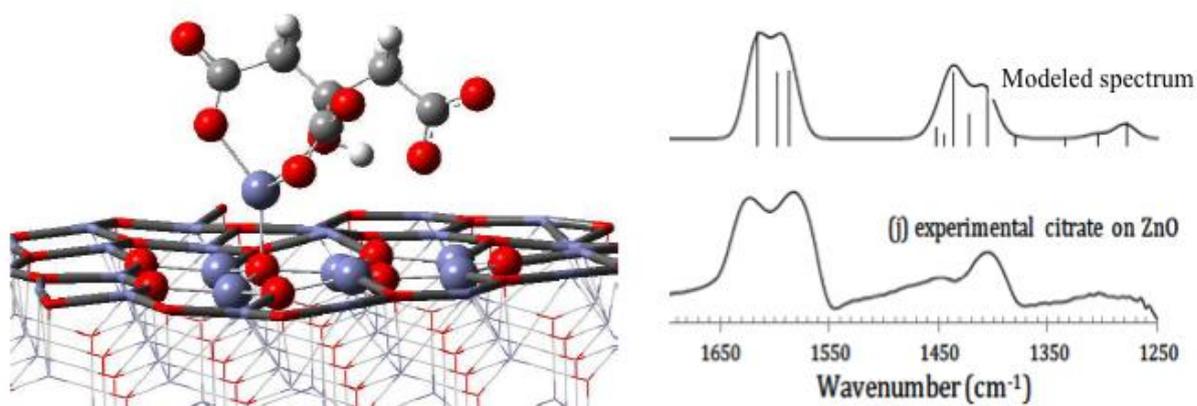


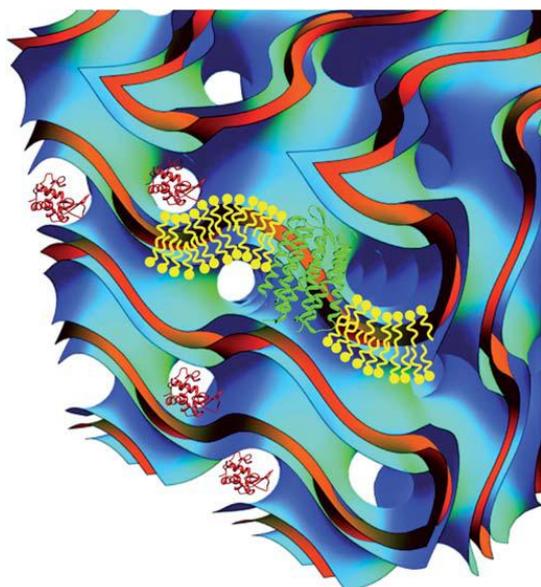
Figure 1. Citric acid bound to ad-atom island on ZnO surface and predicted IR spectra compared to experimentally measured spectrum.

High-throughput Design and Analysis of Bicontinuous Cubic Phases for Protein Encapsulation

Charlotte Conn¹, Leonie van 't Hag², Thomas Meikle², George Feast², Connie Darmanin³, Tu Le², Xavier Mulet², Adrian Hawley⁴, Calum Drummond¹

¹RMIT University, Melbourne, Australia, ²CSIRO, Clayton South, Australia, ³La Trobe University, Bundoora, Australia, ⁴Australian Synchrotron, Clayton South, Australia

Self-assembled lipidic cubic phases are attracting increasing interest as biocompatible carriers of large biomolecules including proteins, peptides, DNA and drugs [1]. A suite of new high-throughput techniques to synthesise and formulate libraries of lipidic mesophases will be described. Structural characterization of these materials for protein and peptide encapsulation was carried out at the SAXS/WAXS beamline at the Australian Synchrotron [2]. High-throughput assessment of functionality for membrane proteins and peptides contained within cubic phases is also presented.[3] We demonstrate how this high-throughput method allows screening of the extremely large variable physiochemical space for *in meso* crystallization, which would be unreasonable to explore using traditional experimental methods. In addition the application of this technique to a wide variety of applications for lipidic mesophases will be described, including pharmaceutical (drug discovery, drug delivery, gene therapy and medical imaging), materials science (biosensors, detergent industries), biology (long-term storage of fragile proteins, crystallization) and chemistry/physics (fundamental surfactant and lipid phase behaviour studies), which are currently restricted by difficulties in handling and characterizing this highly viscous material.



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OC056

Phase transitions in charged cubosome dispersions induced via an electrostatic switch : Applications in Protein Encapsulation and Release

Terry Hartnett^{1,2}, Katherina Ladewig¹, Patrick Hartley², Andrea O'Connor¹, Keith McLean²

¹*Particulate Fluids Processing Centre, Department of Chemical and Biomolecular Engineering, University of Melbourne, Melbourne, VIC, Australia,* ²*CSIRO Energy & Manufacturing Flagships, Clayton, VIC, Australia*

The delivery of the emerging class of biomacromolecular therapeutics, which includes whole proteins and protein fragments, often requires new approaches to encapsulation and formulation, such that their biological activity is preserved, whilst assuring *in vivo* bioavailability.

Dispersed lyotropic liquid crystalline particles such as cubosomes and hexosomes are considered to be promising drug delivery vehicles due to their high aqueous/lipid- interfacial area and tortuous nanostructure which allow for the sustained release of therapeutics¹, however their potential as drug delivery vehicles for protein therapeutics has been limited due at least in part to the energy intensive production methods used in their production, as well as the limited number of approaches which are available for protein encapsulation/formulation.

Recently, we developed a new low energy, biocompatible method of cubosome production, which employs a salt induced 'electrostatic switch' to induce a lamellar to cubic phase transition via the addition of phosphate buffered saline (PBS) to vesicle dispersions containing cationic lipids².

Here, we report on insights regarding the colloidal and nanostructural transitions which arise during/after the electrostatic switch in dispersions incorporating either anionic or cationic lipids/surfactants³. The resulting optimization of dispersion properties which enable the approach to be applied to biomacromolecular encapsulation is also discussed.

Finally, we demonstrate how the technique can be adapted to encapsulate proteins within cubosome dispersions, by adapting an established method of protein encapsulation frequently used to prepare liposome formulations.

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OC057

Bicontinuous Cubic Phases-Based Biosensors

Raffaele Mezzenga

ETH Zurich, Zurich, Switzerland

Bicontinuous lipid cubic mesophases are widely investigated as hosting matrices for functional enzymes to build biosensors and bio-devices due to their unique structural characteristics coupled with their isotropic and transparent nature.

In this talk I will discuss recent progress made in our group towards the understanding of how proteins and enzymes can be reconstituted within lipid cubic phases to yield biosensors for detection of specific target substrates. A few examples will be discussed to illustrate the generality of the approach

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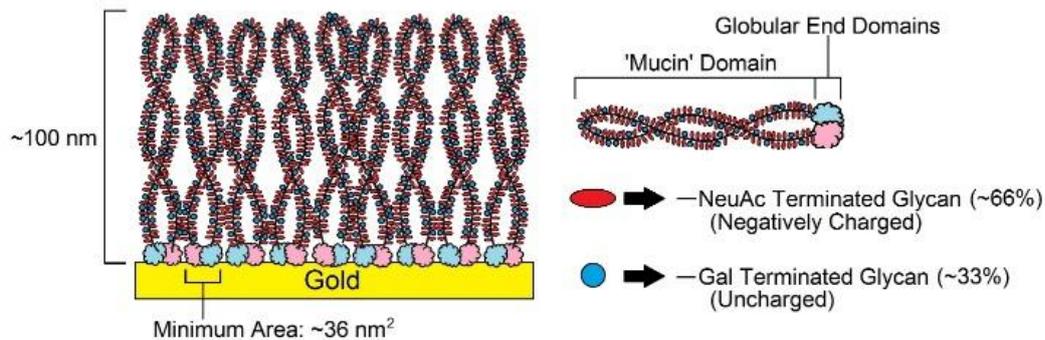
OC058

Lubricin: a biological, universal anti-adhesive with properties comparable to polyethylene glycol

George 'Wren' Greene¹, Lisandra Martin², Agnes Michalczyk¹, Leigh Ackland¹, Roger Horn⁰

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Lubricin is a glycoprotein found in articular joints which has been recognized as being an important biological boundary lubricant molecule. Besides providing lubrication, we demonstrate, using a Quartz crystal microbalance, that lubricin also exhibits anti-adhesive properties and is highly effective at preventing the non-specific adsorption of representative globular proteins and constituents of blood plasma. This impressive anti-adhesive property combined with lubricin's ability to readily self-assemble to form dense, highly stable telechelic polymer brush layers on virtually any substrates and its innate biocompatibility makes it an attractive candidate for anti-adhesive and anti-fouling coatings. We show that coatings of lubricin protein are as effective as, or better than self-assembled monolayers of polyethylene glycol over a wide range of pH and provides a simple, versatile, highly stable, and highly effective method of controlling unwanted adhesion to surfaces.



OC059

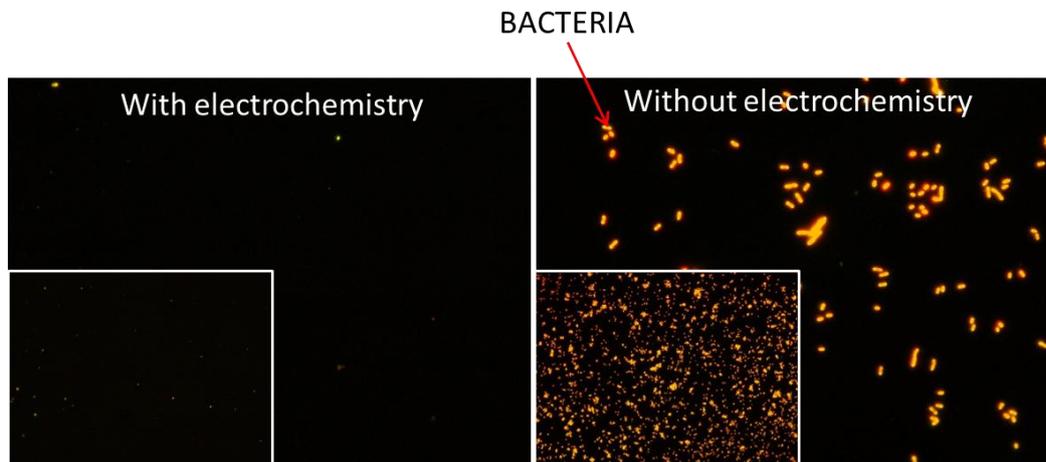
Dynamic and Responsive Polymer Coatings for Prevention of Biofouling

Mikael Larsson, Johan Linden, Ali Yousefi, Simarpreet Kaur, Sait Elmas, Thomas Nann, [Magnus Nyden](#)

University of South Australia, Adelaide, South Australia, Australia

Background: Conventional marine anti-biofouling coatings release biocides. However, these are coming to an end as environmental concerns are rising. We present an effective biocide-free alternative built on the principle of dynamic and responsive polymers. More specifically, two different principles for creating dynamic and responsive polymer coatings have been investigated. The first is based on a polymer to effectively and selectively bind copper from seawater and release it on demand. From an anti-biofouling perspective this enables a flux of copper, a highly effective biocide, across the coating-water interface. That is partly also how the best currently used copper-containing (up to 50 wt %) anti-biofouling coatings on ships and boats work: when immersed in water the coating starts leaking copper, providing a constant flux of biocides across the coating-water interface, which thereby prevents biofouling. However, our coating contains zero % (!) copper initially. When immersed in water it adsorbs the environmentally available copper very effectively and then releases it to prevent biofouling. Our approach thus utilizes a closed cycle of copper across the interface: copper biocides moves in to and out from the coating in a never-ending cycle - a dynamic and responsive polymer coating. Here we present the results from uptake and release studies of copper to and from a very thin layer of a copper specific polymer.

The second principle is based on electrochemical manipulation of a proton pump polymer, a polymer that accepts or donates protons when oxidized or reduced, to locally manipulate the pH and pH gradient at the interface. Cycling between acidic (oxidized state of the polymer) and basic (reduced state) pH provides a changing environment that discourages colonization (biofouling) of the surface by bacteria. Here we present the anti-biofouling results of electrochemical manipulation of a thin layer of a proton pump polymer at a conducting surface. The figure shows fluorescent microscopy images of bacterial colonization of the proton pump polymer surface in the presence (left) and absence (right) of electrochemical manipulation. The external application of a potential for cycling the protonation state of the polymer effectively prohibited bacterial colonization.



Chemically Defined Surface Coatings for Cell Growth

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Control over biomolecule-material and cell-material interactions is critical to the performance of a broad range of applications including cell culture materials, implantable biomedical devices and biosensors. A key design feature for materials for the expansion of cells is that the materials should have both very low non-specific protein adsorption and covalently attached ligands to mediate cell attachment. For cell therapy applications, these materials should be able to function effectively in cell culture media which is chemically defined and animal product free (i.e. serum-free). We have developed a platform, surface initiated polymerisation coating approach¹, which in one step, results in coatings with very low non-specific protein adsorption, i.e. no initial chemical functionalisation or priming steps are required. In addition, the coatings also contain functional groups onto which cell attachment ligands such as peptides can be chemically attached. The approach can be used to produce coatings on many different formats of interest, such as multiwall plates, tissue culture flasks and microcarrier particles.

In this study we have prepared a number of synthetic polymer coatings using a platform grafting from approach to produce materials for the culture of cells. Coatings were formed using a grafting from approach from a monomer feed comprising 10 mole percent acrylic acid and 90 mole percent acrylamide and characterised using a variety of surface analytical techniques including X-ray photoelectron spectroscopy (composition and chemical environment) and direct interaction force measurements via an atomic force microscope (hydrated thickness and elastic modulus). Coupled to these coatings was a cyclic peptide (cRGDfK) which interacts specifically with cell surface $\alpha_5\beta_1$ integrins cells only. These surfaces were found to be highly suitable for the attachment and growth of murine L929 fibroblasts, human mesenchymal stem cells (hMSCs) and human embryonic stem cells (hESCs). Furthermore, in the case of hMSCs the surfaces were used to expand the cells over three passages in three different media (two media were serum free). The hMSCs were characterised by their ability to differentiate into adipocytes, osteocytes and chondrocytes as well as maintenance of cell surface markers typically used to define hMSCs.

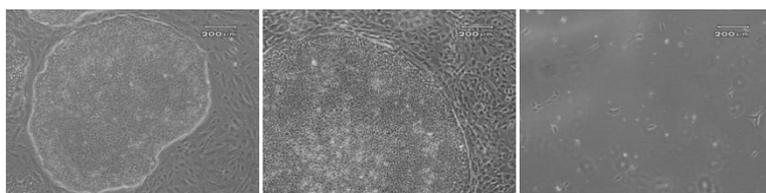


Figure 1: Human embryonic stem cells growing on (a) MatrigelTM, (b) chemically defined surface with coupled cRGDfK bioactive peptide and (c) chemically defined surface with coupled cRADfK non-bioactive peptide in chemically defined mTeSR cell culture media after 7 days

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OC061

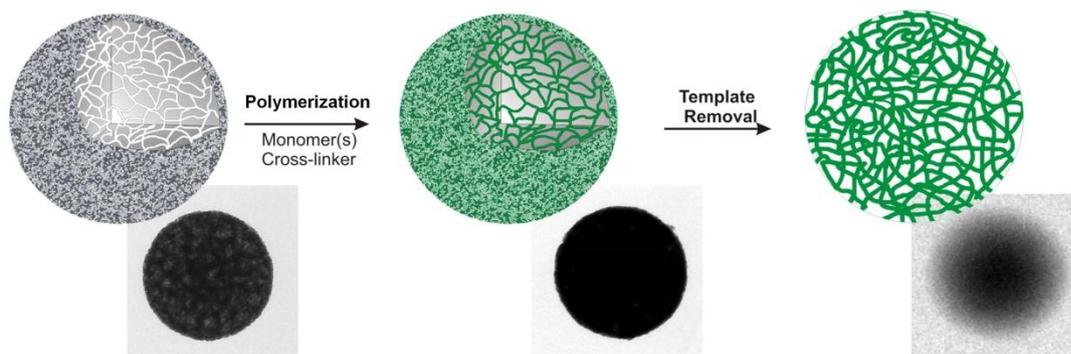
Surface-Initiated Polymerization within Mesoporous Silica Spheres for the Modular Design of Polymer Particles

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Through combined efforts in nanotechnology and biomedicine, nanoengineered particles have emerged as potential candidates to enhance the diagnosis and treatment of various diseases. Polymer carriers with tailor-made properties and functionalities have received growing interest in nanomedicine.

We report a facile 'one pot' approach for the preparation of functional polymer replica particles via surface-initiated polymerization in mesoporous silica templates. Using a redox-responsive cross-linker allowed the disassembly of these particles in a reducing environment. The incorporation of functional comonomer groups was demonstrated by conjugating dye and drug molecules onto the replica particles. Biomedical relevant particles, made of poly(methacryloyloxyethyl phosphorylcholine) (PMPC) and poly[oligo(ethylene glycol) methyl ether methacrylate] (POEGMA), exhibited negligible cytotoxicity and very low association to human cancer cells (below 5%). The reported charge-neutral particles represent a modular and versatile class of highly functional carriers with potential applications as drug delivery systems.



Evaluating Metal Nanoparticle Dissolution Kinetics; Assessing the Fate of Silver Nanoparticles in Surface Water

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During the last decade, the production and use of nanomaterials have experienced a drastic increase, resulting in a potential risk of their release into the environment. The interplay between nanoparticle size, dissolution rate, agglomeration, and interaction with the sample matrix is critical to appropriately characterising the risks associated with engineered and naturally occurring nanomaterials may pose to environmental health. Herein, we seek to precisely track changes in nanoparticle size, associated dissolved metal concentration, and determine the polydispersity of a nanoparticle sample, all at dilute concentrations in complex solutions using single particle ICP-MS (SP-ICP-MS) in conjunction with more limited traditional techniques such as dynamic light scattering (DLS). Because dissolution rate is surface-area controlled, the time to complete dissolution is highly dependent on the initial and (potentially stable) intermediate particle sizes. By measuring the change in particle size, as well as the evolution of $\text{Ag}^+(\text{aq})$ in solution, potential pitfalls related to loss of Ag^+ to experimental materials and to other environmental surfaces, such as suspended sediments or biota in the case of complex matrices, may be avoided and or differentiated.

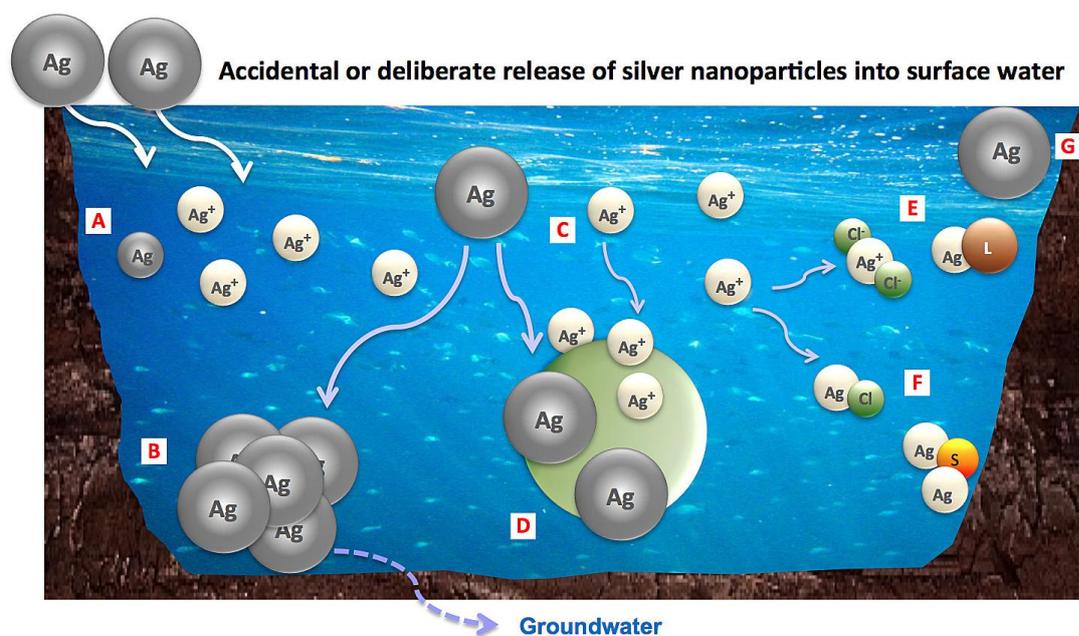


Figure 1. Possible fates of silver nanoparticles in surface waters: (A) Dissolution process leading to free ions release and smaller particles; (B) Aggregation into larger particles, which may settle out of the water, depending on the aggregate size; (C, D) Adsorption of released Ag^+ and $n\text{Ag}$, respectively, onto other solids present in the water; (E) Formation of soluble complexes; (F) Reaction with other components in the water, which may result in precipitation; (G) $n\text{Ag}$ remaining stable.

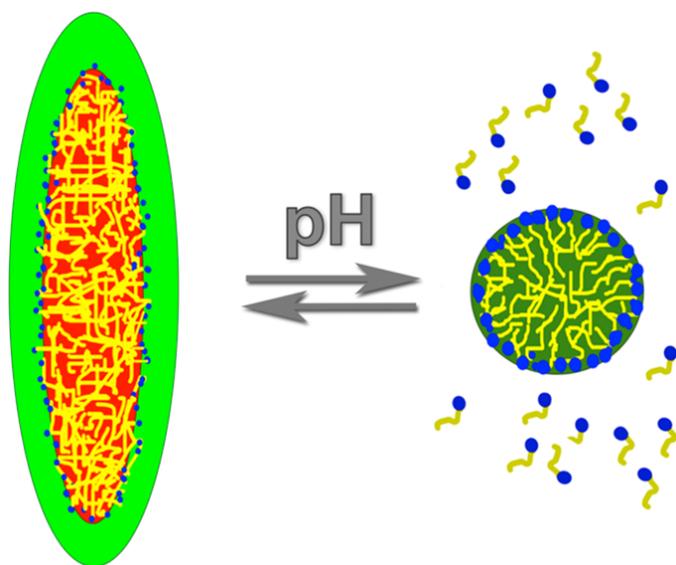
OC063

Small-Angle Neutron and X-Ray Scattering of pH-Responsive Micelles Based on Caprylic Acid

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Free fatty acids play a vital role as fuel for cells and in lipid metabolism. During lipid digestion in the gastrointestinal tract, triglycerides are hydrolyzed resulting in the amphiphilic products free fatty acids and monoglycerides. These components, together with bile salts, are responsible for the transport of lipids and poorly water soluble nutrients and xenobiotics from the intestine into the circulatory system of the body. In this study we show that the self-assembly of digestion products from medium chain triglycerides (tricaprylin) in combination with bile salt and phospholipid is highly pH responsive. Individual building blocks of caprylic acid within the mixed colloidal structures are mapped using a combination of neutron scattering combined with both solvent contrast variation and selective deuteration as well as synchrotron-based small angle X-ray scattering (1). Modelling of the scattering data shows transitions in size and shape of the micelles in combination with a transfer of the caprylic acid from the core of the micelles to the shell or into the bulk water upon increasing pH. The results help to understand the process of lipid digestion with a focus on colloidal structure formation and transformation for the delivery of triglyceride lipids and other hydrophobic functional molecules.



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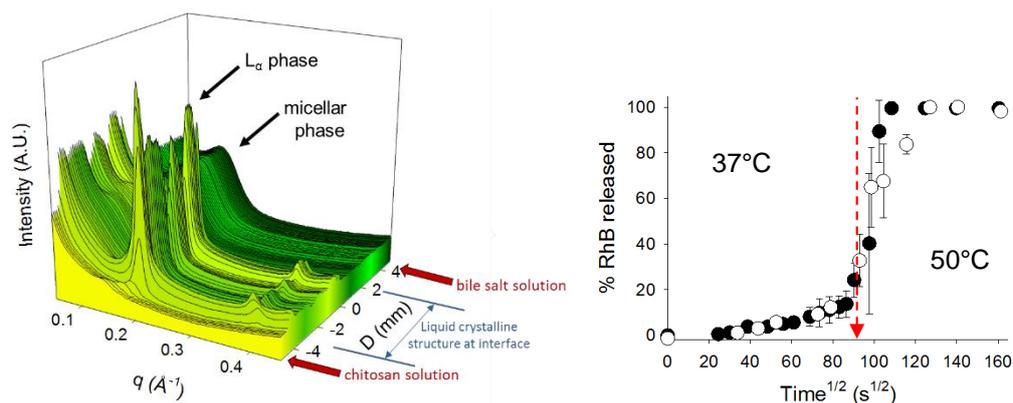
Using spatially-resolved synchrotron scattering for the design of novel stimuli responsive drug delivery nanomaterials

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Unlike the coacervated material formed on interaction of oppositely-charged polymers in eg. layer by layer assembly, the interface between oppositely-charged surfactant and polymer solutions can generate rich self-assembled structures, not necessarily found in the binary surfactant-water phase diagram. We have been using spatially-resolved scattering approaches to understand the structures formed at these interfaces. Specifically by contacting the solutions in a flat capillary cell to form a well-defined interface, SAXS can be used in a 'scanning' mode, to determine the changes in self-assembled structure with 100 micron resolution through the interface. The structure can then be manipulated through changes in variables such as temperature or pH to yield stimuli responsive materials that can be used to form eg. nanostructured capsules for controlled release applications. Structures formed at the interface of the anionic co-polymer poly(acrylamide-acrylic acid) (PAAm-AA) and cationic CTAB as a pH responsive system, and chitosan and bile salt as a biocompatible positive polymer/negative surfactant pair were studied. Capsules were also formed from the materials containing a dye by introducing droplets of one liquid into the other, and monitoring the inherent and stimulated release of the dye from the capsules.

The bile-salt + chitosan system formed a lamellar structure at the interface (figure below) [1]. Increasing the temperature of the system above physiological temperature led to destruction of the lamellar phase and stimulated release of the encapsulated dye. The PAAm-AA + CTAB system on the other hand formed a hexagonal phase at the interface. Reduction of the solution pH from pH 7 to pH 2 (through the pKa of the polymer) in that case also led to destruction of the self-assembled interface and complete release of encapsulated dye. These systems indicate the potential for new stimuli-responsive materials that have been enabled by the spatially-resolved scattering capabilities at the Australian Synchrotron.



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OC065

Discontinuous swelling of pNIPAM microgels by light and Neutron Scattering

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The swelling of polymer gels is a fundamental and classic problem in polymer physics and probably its most interesting feature [1]. Whereas macrogels exhibit continuous or discontinuous volume transition depending on gel composition, their microscopic counterparts -micro or nanogels- typically undergo a continuous transition irrespective of the polymer nature or experimental conditions [2]. We report here the conditions to achieve the discontinuous transition in a slightly cross-linked poly(N-isopropylacrylamide) microgel that usually shows a continuous size-transition against temperature. By using water-ethanol mixtures as solvent we find that the volume transition associated with temperature changes qualitatively from continuous to discontinuous as a result of the cononsolvency phenomenon. The modifications on the internal polymer structure along the discontinuous transition are investigated by means of small angle neutron scattering. We identify the critical isobar on the phase diagram and measure the different critical exponents using light and neutron scattering. The results indicate the universality class of the microgel volume transition is that of a three-dimensional Ising system.

This work has been funded by the Spanish Ministerio de Economía y Competitividad/FEDER (project MAT2011-28385), Andalusian Government/FEDER (Project P010-FQM 06104) and EU-COST-Action CM1101.

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OC066

Bond Compression, Breakage and Cage Melting: A Fresh Look at the Shear Rheology of Strongly Flocculated Suspensions

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Suspension shear rheometry typically consists of measuring the shear yield stress and then the steady-state viscosity as a function of rate or stress. This facilitates using constitutive descriptions such as the Bingham or Herschel-Bulkley models. However, such descriptions are overly simplistic. For many suspension processing applications such as flow start-up in pipelining or the flow of slurries in minerals tailings operations, an improved understanding of shear rheology is needed.

The deformation and flow of strongly flocculated suspensions are governed by the strength of the inter-particle interactions and the number of interactions. As such, given an appropriate measurement technique, one would expect to see aspects of bond deformation and bond breaking. In this work, we have subjected a model system (roughly 4 μm calcium carbonate that is strongly flocculated at its iso-electric point) to a broad range of controlled stress and controlled rate experiments in a vane-in-an-infinite cup geometry. The wide gap geometry ensures minimal wall effects such as slip and jamming. Careful examination of the transient behaviour has produced a rich understanding of the suspension response. For example, constant stress creep experiments show linear viscoelasticity, non-linear softening and time-dependent yielding. Constant rate experiments show linear behaviour at very small strains, strain hardening corresponding to bond compression and then strain softening corresponding to bond breaking. For low concentrations, yielding occurs at strains corresponding to bond breaking whereas at high concentrations, yielding occurs at strain unity, corresponding to cage melting where particles are moved one particle distance in order to yield. The yielding behaviour in constant rate is rate dependent, showing that stress is not the relevant parameter to describe suspension behaviour.

The ability to measure the effects of inter-particle forces enables the development of suspension rheology from its current empirical state to a quantitative science where constitutive descriptions can incorporate the microscopic properties of the suspension to describe the bulk behaviour. Such a progression would enable the prediction of suspension processability when particle properties are changed, for example.

OC067

Dynamics and Structure: A Study of Arrest in a Non-Aqueous Colloidal System

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Across the globe the use of biodiesel as a fuel is increasing whilst the long term effect that this has on the engine lubricant, and in turn the engine, remains unknown. Combustion of biofuels introduces new contaminants to the lubricant, namely ethanol, acetic acid and additional water. The impact these small polar species have on one class of engine oil additive, overbased detergents, has been studied using a range of techniques, including small angle neutron scattering (SANS), dynamic light scattering and rheology.

Overbased detergent particles are typically less than 10 nm in diameter. They comprise a metal carbonate core and surfactant shell. These particles are included in the lubricant to neutralise acids and prevent deposit formation on the metal parts. The effect of the contaminants is largely determined by the identity of the surfactant molecule.

When water was added to samples of sulfonate overbased detergents, sedimentation of surfactant and some metal carbonate occurred in the following 24 hours. Upon the addition of water to solutions of a particular salicylate overbased detergent in n-dodecane, gelling occurs over a period of weeks. The dynamics of gelling and mechanical properties of the gel have been found to vary depending on the volume fraction of particles and the volume of water added. The arrest is hypothesised to be due to a bridging space spanning structure, induced by the formation of aggregates of surfactant. Varying the particle volume fraction, volume of contaminant and free surfactant concentration have all been found to have an impact on the arrest.

Revisiting Kynchian Analysis of Gravitational and Centrifugal Settling for Strongly Flocculated Suspensions

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Solid-liquid separation involving strongly flocculated suspensions is important in a large range of industrial applications, including mineral processing and wastewater treatment and disposal. Development of theoretical descriptions of solid-liquid separation, or dewatering, has allowed modelling of different dewatering behaviour and optimisation of dewatering device design. Kynch (1952) developed a dewatering theory for interpreting experimental gravitational settling results at high particle concentrations but it failed to account for compression of the settled material [1]. Buscall and White (1987) introduced a fundamentally rigorous dewatering theory for colloidal suspensions able to account for this material compressibility [2]. The theory uses two key parameters; the extent of dewatering or Compressive Yield Stress, $P_y(\phi)$, and the rate of dewatering or Hindered Settling Function, $R(\phi)$.

The hindered settling function, $R(\phi)$, is a material property dependent on the solids volume fraction, ϕ , that quantifies the interphase drag or hydrodynamic force on colloidal suspensions. This can be applied to a solid moving through liquid during settling or liquid moving through solids in the case of cake consolidation. There are existing methods capable of determining $R(\phi)$ from gravitational settling tests [3] and centrifugal settling tests [4] that have been shown to accurately model dewatering behaviour. The work of Usher et al. (2013) assumes certain aspects of centrifugal sedimentation behaviour that only approximate model predictions. A more rigorous analysis using the method of characteristics is conducted in this analysis. This study extends the work of Lester et al. (2005) by applying the same methodology to settling under a centrifugal force.

The model suspensions used in this study were wastewater treatment sludges, which are dewatered industrially using a wide variety of operations from basic sedimentation to high-speed centrifugation. $R(\phi)$ values were extracted for these materials over a large range of volume fractions. These results enable more rigorously valid characterisation of material dewaterability from batch gravitational and centrifugal settling tests, thus providing useful information for suspension processing.

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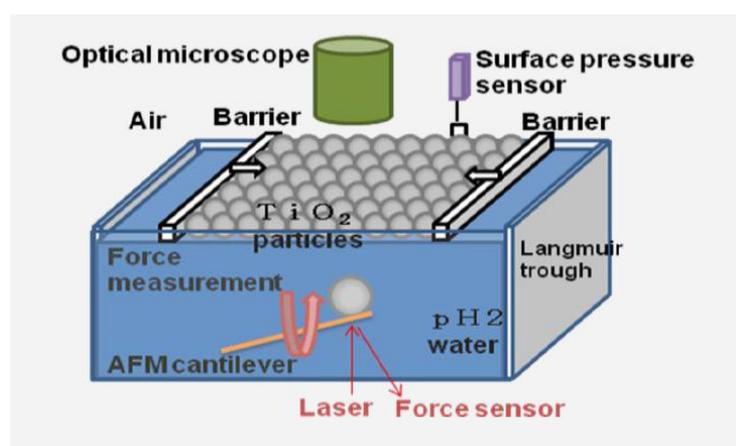
Determination of the Physical Properties of a Particulate Langmuir Monolayer at an Air/Water upon Collision with an External Particle

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Oil in water emulsions can be stabilized by the adsorption of particles at the oil/water interface of the emulsion. Here, we determined how the size of the particles and their packing density affects the physical properties of a model emulsion, after another material has collided with it. We achieved these studies by modelling a particle-stabilized emulsion with a monolayer of bare TiO₂ particles at an air/water interface [1]. The Monolayer Particle Interaction Apparatus (MPIA) was used to obtain surface pressure-area isotherms of the particulate monolayers at an air/water interface and to directly study the forces between the TiO₂ monolayers at an air/water interface and a micro-sized TiO₂ particle (probe) in the subphase. The effect of the bringing the micro-sized TiO₂ probe particle in the subphase in and out of contact with the TiO₂ monolayer on the particle packing in the monolayer was observed by optical microscopy, while the forces were simultaneously measured. The effects of the particle size on the physical properties of the monolayer were investigated by using particles with a diameter of 75 nm, 300 nm, 3 μm and 10 μm.

We found that an increased packing density acted to increase the stiffness of the monolayer and to decrease the adhesion. The increased stiffness was explained by the stronger inter-particle attractions, due to van der Waals and capillary interactions. The adhesion decrease was explained by the decreased wetting of the probe, caused by the decrease in the bare air/water areas as the islands of TiO₂ particles converged with an area decrease. We also saw for densely packed monolayers that the stiffness of the particulate monolayer could be controlled by the size of the particles used in the monolayer. In general, the stiffness increased with a particle size increase. This result was explained by the particle-particle lateral capillary interactions, which increase with a particle size increase. The adhesion between the particulate monolayer and the incoming particle (probe) was seen to be controlled by their relative size difference between the particles in the monolayer and the probe. The adhesion increased as the size of the probe became larger than that of the particles in the monolayer. If the particles in the monolayer are smaller than the probe particle, then the monolayer acts as a soft material that can cover the probe particle. However, if the particles in the monolayer are bigger than the probe particle, then the monolayer cannot cover the probe particle and acts as a hard material, i.e., non-deformable monolayer.



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Quantifying the Hydrophobic Interaction between Extended Surfaces via Dynamic Interactions Involving Oil Drops and Bubble

Derek Chan¹, Rico Tabor³, Chu Wu¹, Raymond Dagastine¹, Franz Grieser¹, Erqiang Li⁴, Ivan Vakarelski⁴, Siggidur Thoroddsen⁴

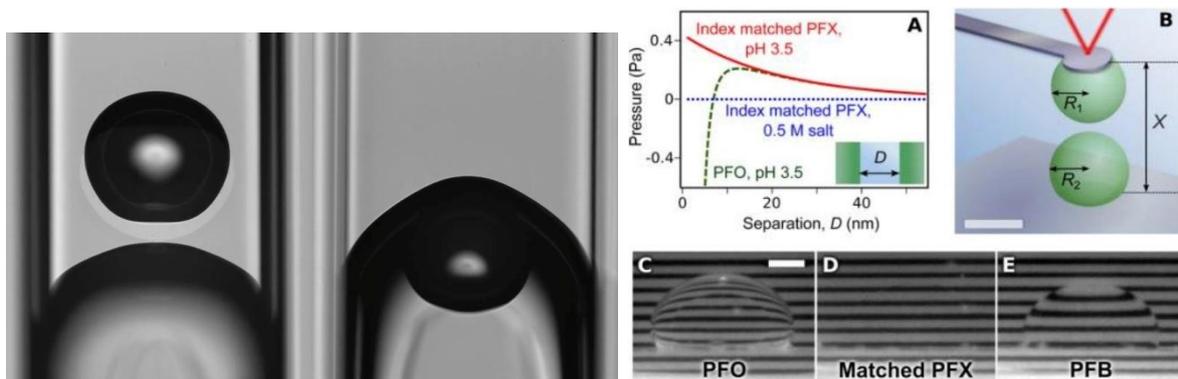
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For over past 3 decades, there have been many attempts to quantify the separation dependence of the hydrophobic interaction between extended surfaces. The most prolific approach has been to undertake direct force measurements between hydrophobised solid surfaces using the Surface Forces Apparatus or the Atomic Force Microscope. This approach affords the capability of being able to measure the separation between the solid substrates and the flexibility in studying different ways to render the otherwise hydrophilic solid surfaces hydrophobic -- such as by physical adsorption of hydrophobic long chain surfactants or by chemical attachment of hydrophobic molecules or polymers.

However, the results have been spectacularly varied in that the range of the additional attraction, above that expected from classical DLVO theory, has been reported to vary between ~ 1 nm to $100\ \mu\text{m}$. The explanations advanced for this variability ranged from being due capillary bridging between nano-bubbles that appear to form on hydrophobised surfaces to the formation of mobile charged patches resulting from the 2D association of adsorbed charged surfactant and the exposed surface charges of the solid substrate. Although such results are interesting, they may not be directly relevant to understanding the hydrophobic interaction between extended non-aqueous extended surface such as oil drops or bubbles.

This presentations reports observations and analysis of the dynamic, that is, velocity- and time-dependent, collisions between a bubble and a fluid-fluid interface and collisions between inert oil droplets.

The aim is to uncover the nature of interaction forces between molecularly smooth and inert extended bodies beyond that due to DLVO forces through careful material selection and control of solution conditions, and crucially, to avoid extraneous effects that arise from working with hydrophobised solid surfaces.

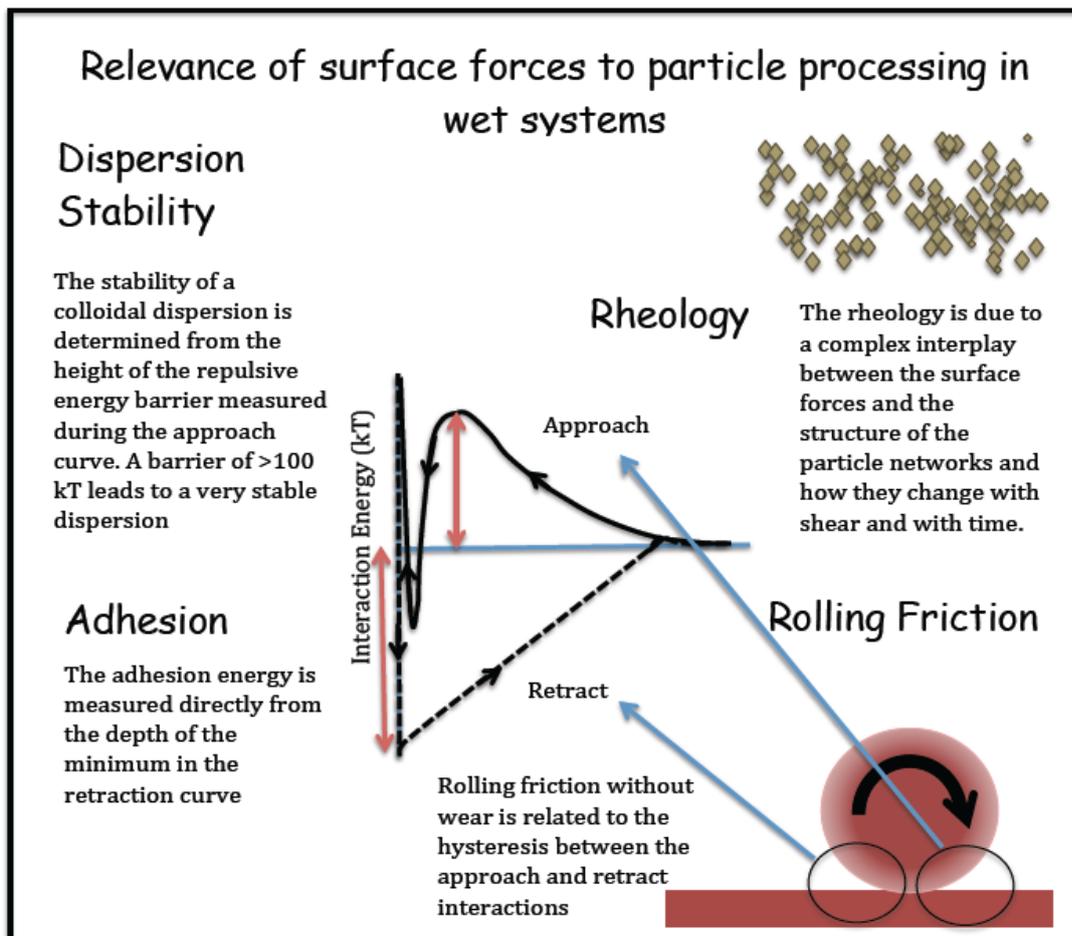


Surface Forces between surfaces produced using Atomic Layer Deposition

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Surface forces play a fundamental role in particle processing as they control the stability, adhesion, friction and rheology of particulate systems and information on all of these can be obtained from an analysis of the normal forces measured between particles. Therefore particle processing at all stages can be informed by knowledge of the forces between the constituent particles. For wet particles systems, the interaction forces between two particles can rarely be predicted from theory, but rather requires experimentation or direct measurement. This requires that the surfaces used have the same surface properties as the particles. In practice this is rarely possible, as surface force measurements require surfaces with extremely low roughness and precise geometry and the majority of materials do not conform to these requirements. To address these challenges we produce surfaces of low roughness and controlled chemistry using Atomic Layer Deposition (ALD) and are developing methods to calculate and understand the influence of surface roughness on the measured forces. Here we report the forces between hafnia surfaces produced by ALD and show that like ALD produced titania surfaces and silica surfaces, the expected van der Waals forces at high pH are not manifest, suggesting that most real surfaces have unexpectedly repulsive surface forces at high pH and small separations. This will fundamentally alter how these particulate systems behave when being processed, reducing the adhesion and the friction and enhancing the stability compared to the expected interaction from DLVO theory.



OC072

Deuteration effects on “Soft” Proteins

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In work to understand the effects of deuteration on the “soft” protein human serum albumin we have found some potentially general phenomena which have possible consequences for the use of deuteration in some contrast variation experiments for neutron scattering.

Dynamic light scattering, small angle neutron scattering and UV circular dichroism combined with eight different combinations of solvent change from H₂O to D₂O; full deuteration or not of the protein itself and the effect of the fatty acid ligand have been used to study the aggregation of the proteins and their interaction with the surface of nanoparticle silica.

OC073

Self-assembly and Gelation of Conjugated Polymers in Organic Solvents

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Conjugated polymers are shown to self-assemble in organic solvents forming fibers and branching networks that could be ideal structures for efficient photovoltaic devices and organic electronic applications. The temperature-induced sol-gel transition of these semiconductor materials is shown to directly correlate with large changes in optical, electronic and mechanical properties. This presentation outlines recent work using combined small angle neutron scattering experiments (rheology-SANS and dielectric-SANS) that have contributed to increasing our understanding of the nanoscale processes that control the formation and dissolution of these unique polymer networks. Processing of the semiconductor organogels as emulsion dispersions has also been demonstrated and prototype solar cell devices have been fabricated from networked materials. These results and future prospects for using gelation to produce efficient and stable organic solar cells will also be discussed.

OC074

SANS and Multiscale Molecular Modelling of Polymer-Drug Conjugates

Glib Meleshko, David Willock, James Platts, [Alison Paul](#)

Cardiff University, Cardiff, UK

Polymer-drug conjugates (PDCs) are advanced drug delivery systems with particular potential as anti-tumoral therapeutics, where the use of a biocompatible, water-soluble polymer carrier linked to a powerful chemotherapeutic molecule affords increased solubility of a hydrophobic drug, enhanced circulation times in the body and concentration of the active molecule to tumour sites where it is selectively released, thereby reducing toxicity and side-effects.

There is increasing recognition that the conformation adopted by these conjugates during transport and delivery processes can significantly influence therapeutic performance [1]. Understanding the interplay between polymer, linker, drug and conformation is a challenge [2,3]. In this work small-angle neutron scattering methods have been used to understand, predict and ultimately control the conformation adopted by model conjugates to provide target conformations. To accelerate development of conjugates with potential clinical use, we have developed molecular modelling techniques in an attempt to accurately simulate the solution behaviour of polymer-drug conjugates, with the intention of providing a fast-throughput screening mechanism as an alternative to synthesising large libraries of materials.

Quantum chemistry calculations on bond rotations in HPMA dimers have been carried out to determine the correct force field parameters for simulation of larger structures. Ab initio calculations were carried out in the gas phase, and with simple reaction field solvent models. Molecular dynamics simulations were then used to investigate larger HPMA oligomers and eventually polymers up to ~35000 Da using reaction field, distance and explicit solvent models to determine the correct solvent model and explore computational limits. In-house analysis tools were applied to determine the shape of the structures formed (based on an ellipsoid analysis from the centre of mass), and ultimately to determine the distribution of different atom types throughout the structure.

In addition, a distance-distribution analysis from the centre of mass was developed and by labelling different atom types it was possible to determine the distribution of different atom types throughout the structure. In ongoing work, these protocols are being developed to provide a less computationally expensive methodology that will allow inclusion of explicit solvent molecules and study of larger and more complex conjugate molecules. Significant development work is required, but the methods have the possibility to provide atomic level information on conjugate structures adopted in solution.

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OC075

Interactions of Solute Molecules with an Interface by Medium Angle Diffraction

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In this study we present a method for determining the profile of solute molecules confined between two interfaces. Stacks of oriented bilayers supported on a quartz slide are useful a model system to study the interactions of different molecules with planar interfaces. The samples are effectively one dimensional crystals. In this case the unit cell includes the bilayer and inter layer solution and any molecules localized within this structure. Fourier methods may be used to reconstruct the scattering length density profile of the unit cell from neutron diffraction measurements thus yielding information about the distribution of components of the solute within a unit cell. Deuteration of the sample components can be used for phasing of the Fourier reconstruction or to provide contrast between components in bilayer stacks¹. We discuss the application of selective deuteration of various components of the lipid bilayer and the application of such methods to systems of higher dimensionality such as hexagonal and cubic phases and the use of anomalous (energy dependent) diffraction as a means of obtaining phase information.

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OC076

Visualisation of yielding propagation

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Particulate suspensions commonly exhibit yielding behaviour where at some critical point it behaves as a fluid rather than a solid. Understanding the yielding behaviour of particulate suspensions is important for industrial purposes, such as pipeline design, mixing and slumping. This yielding behaviour can be measured by performing a creep (constant stress) test using a controlled-stress rheometer with a vane-in-an-infinite-cup. The vane and wide gap configuration minimizes the wall slip effects and jamming. A series of constant shear stresses are applied to the suspensions for a period of time while the resulting deformation is measured for each stress. For concentrated and/or strongly flocculated suspensions, yield is typically stress and time dependent. The radius of yielding is initially at the tip of the vane but then moves outwards to some steady-state radius. However, since the vane is submerged in what is usually an opaque suspension, it is impossible to see the propagation of the yield front. Also, several techniques such as particle tracking, video microscopy, Rheo-NMR, cannot be used to track this yield radius propagation.

To specifically investigate the yield front propagation, creep experiments with the vane at the surface of the suspension were performed. The suspension was marked with a straight line of a tracer. Using video analysis, it was possible to observe the deformation as a function of radius and hence the change of yield radius with time. Since the stress decays with the radius squared, the yield radius as a function of time could be converted to yield time as a function stress. Two different tracers, food dye and glitter particles, were used. It was found that the vane-at-the-surface and the submerged-vane creep tests have the same deformation behaviour (accounting for differences in torque). However, there were deviations in the yield propagation for the food dye and the glitter particles. This suggests that the glitter particles were not wetted by the suspension and were subject to surface effects. The surface results did not correspond exactly with the submerged results but instead showed yielding out to a greater radius. This is also shown in the deviations in the yielding times at lower stresses for the vane-at-the-surface with glitter particles and submerged-vane creep experiments.

OC077

Competitive Molecular Adsorption Mechanisms and Particle Stability Studied by Rheology, Adsorption Isotherm, Radiation Interaction, and Atomic Force Microscopy.

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Nanoparticle TiO₂ finds application as an inorganic sunscreen active as a result of its interaction with UV radiation. It is crucial that the particles are present as discrete nanoparticles so that scattering of visible light is minimised and UV attenuation is optimised; thus stabilisation is essential to prevent particles from aggregating. This stability is usually achieved using adsorbed – often polymeric – surfactants for particles suspended in a medium. The choice of the stabiliser will affect not only particle stability but also the rheological properties that affect acceptability of the dispersion for the application.

The objective of this work was to use rheological techniques to characterise dispersion properties to determine suitability of stearic acid-based dispersing agents for TiO₂ nanoparticles in non-aqueous media. Application of the semi-empirical Krieger-Dougherty model to dispersions of increasing solids volume fraction allowed us to identify appropriate dispersant molecular weight to achieve highest solids loading. This model was also applied to identify the optimum solvent conditions that provide a balance between chain extension in good solvent conditions and the increased effective solids volume fraction as a result of large stabilising layer thickness (δ), with the large δ that results from high density packing at the particle surface in relatively poor solvents.

The rheological behaviour of the suspensions was compared with other techniques for characterising dispersion properties. This included adsorption isotherm measurement using a technique developed employing gel permeation chromatography (GPC) which provided insights into the molecular weight-controlled adsorption dynamics. Specifically, GPC enabled us to observe preferential adsorption of the smaller molecules in systems of distributed molecular weight and mixed molecular weight systems. This is contrary to the behaviour of multi-segmented adsorbing polymers often used for particle stabilisation that display a direct relationship between molecular weight and strength of adsorption. Thus, the mechanisms of adsorption of molecules to the particle surface could be deduced and controlled.

Particle stability and the quality of the dispersion were investigated using UV/vis spectrophotometry, exploiting the nature of the interaction of the particles with radiation in this wavelength region. Direct measurement of particle stability was evaluated using atomic force microscopy. The distance of repulsive interaction of surfaces coated with dispersants of various molecular weights was compared with the predictions made from rheological and adsorption isotherm techniques and was found to be in good agreement.

The combination of these techniques has provided valuable insights into the stabilising mechanisms in play for fatty acid dispersing agents. This knowledge allows for optimised dispersion properties and the ability to predict stability in multi-component systems, such as the complex cosmetic formulations in which these dispersed particles are often incorporated.

Aggregation Rates of Latex Particles in Ionic Liquids

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We have measured aggregation rates of polystyrene latex particles in water miscible ionic liquids (ILs) by light scattering techniques.¹ As shown in Figure 1, one observes very slow aggregation at low IL concentration while the aggregation become fast as the IL content increases indicated by high absolute aggregation rate coefficients. This behaviour is similar to simple salts and can be qualitatively rationalized with the classical theory developed by Derjaguin, Landau, Verwey and Overbeek (DLVO). Further increasing the IL-to-water molar ratio, the aggregation proceeds again very slowly and as a consequence, one can formulate very stable colloidal suspensions in ILs. If we normalize the absolute aggregation rate coefficients by the viscosity of the systems, two generic mechanisms that are responsible for this stabilization can be identified. Viscous stabilization mechanism is the most important in highly viscous ILs and originates from the slowdown of the

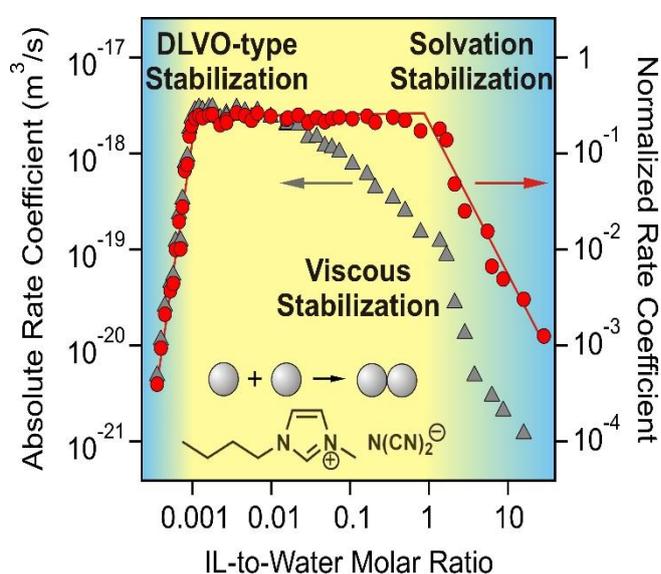


Figure 1. Absolute and normalized aggregation rate coefficients of amidine latex particles at different IL-to-water molar ratios. The schematic representation of the doublet formation and the structure of IL are in the inset.

diffusion controlled aggregation rate due to slower diffusion in a viscous liquid. This effect leads to smaller absolute aggregation rates, but the high normalized rate coefficient values indicate that the aggregation is still driven by diffusion of the particles. Solvation stabilization mechanism is system specific, but can lead to a dramatic slowdown of the aggregation rate in ILs. This mechanism is probably related to repulsive solvation forces that are operational in ILs due to strong layering close to the surfaces. These two stabilization mechanisms are suspected to be generic, as they were operational in different ILs, for particles differing in surface functionalities and their size. Nevertheless, we suspect that in ILs containing tetrafluoroborate anions the principal mechanism is solely viscous stabilization and solvation stabilization is absent. On the other hand, ILs containing dicyanamide or thiocyanate anions together with imidazolium, pyridinium or pyrrolidinium derivatives as cations tend to stabilize suspensions by both mechanisms.

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Particle aggregation mechanisms in ionic liquids. *Phys. Chem. Chem. Phys.* **2014**, *16*, 9515-9524.

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Innovative Colloidal Processing of Multi-scale Porosity Ceramic Materials.

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Multi-scale porous ceramics have applications as ultra high temperature insulation, filtration, electrodes for batteries/fuel cells and catalyst supports. The control of the processing conditions is key to achieve the desired amount, size and shape of porosity for each of these applications. In this work, highly porous ceramic materials have been produced by four different processing routes: a) particle stabilized foams plus gelcasting, b) ice templating, c) replica and d) partial sintering (Figure 1). The exhaustive control of the interparticle forces between particles and understanding the interaction between additives and powder surfaces have been key in developing highly porous oxide and non-oxide ceramics. The study of the rheological behaviour of the different suspensions used in this work has been crucial to optimize the processing conditions. Multi-scale porous ceramics with porosities between 75-92% have been prepared by combining the different types of porosity mentioned above have been produced. The multi-scale porous microstructure present a mixture of open and closed porosity and several pore sizes in the same material. The use of these colloidal processing techniques also enable the preparation of large complex-shape components with the same customized tailored porous microstructure minimizing the formation of drying cracks.

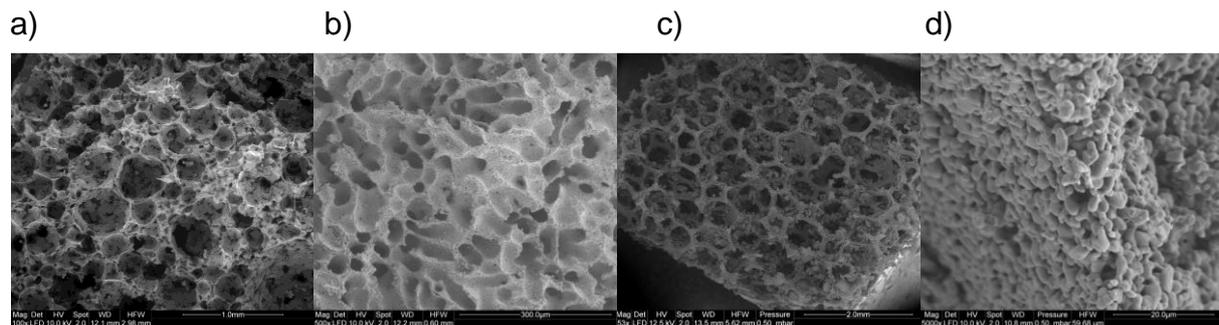


Figure 1. SEM images of the different types of porous ceramic materials produced by the particle stabilized foam and gelcasting (a), ice templating (b) replica (c) and partial sintering (d) methods.

OC080

Computer Simulation of Static and Dynamic Behavior of Micelles in Pluronic Mixture

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Co-micellization behavior for the binary mixture of Pluronics (triblock copolymers) in dilute aqueous solutions was investigated using dissipative particle dynamics simulations. Four different cases were chosen to represent the polymers of different block lengths with varying similarity/dissimilarity: F127/P123, F127/P105, P123/P84 and F127/L64. Both the micelles consisting of a single species of Pluronics (pure micelles) and mixed micelles co-exist for all the cases in the concentration range studied. When the two species are at near equal concentrations in solution, the number fraction of mixed micelles could reach a maximum with traces of pure micelles of both species. In the case of F127/L64, L64 was found to participate in co-micellization even below its CMC.

The mixed micelles are ellipsoidal and their composition is proportional to the prescribed concentration of Pluronics in the solution. The shorter chains take the position near the periphery of the core of micelles. In addition, the dynamics of chain exchange between micelles at equilibrium was investigated. Pure micelles were observed to exhibit multiple relaxation behavior in contrast to micelles of diblock copolymers, for which the time correlation is often explained using a single exponential decay function. For mixture cases, the relaxation times for the mixed micelles are proportional to the concentration of Pluronics in the solution.

Structural Forces in Deformable Systems under Dynamical Conditions

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Structural forces arise from the particulate nature of matter and are thus a ubiquitous part of the physical world. When two surfaces are driven together through a liquid medium, they may experience a series of repulsive and attractive forces due to the expulsion and structuring of the liquid molecules.¹ Similar observations have been made with systems containing small nanoparticles dispersed amongst micron-scale deformable drops in a liquid whereby the large drops experience structural forces due to the ordering of the nanoparticles.² In this presentation, a method of calculating the structural disjoining pressure of spherical surfactant micelles based on their physical properties will be outlined. This technique utilises the Hayter-Hansen-Penfold and Ginoza method to determine the structure factor and hence the effective micelle concentration which is then substituted into a density functional theory parameterisation scheme developed by Evans³ to calculate the structural disjoining pressure. This information can then be substituted into the Stokes-Reynolds-Young-Laplace model which enables us to study the impact of both the Laplace Pressure and the hydrodynamic pressure on the interaction of oil drops driven through a high concentration spherical surfactant micellar solution under dynamical conditions.

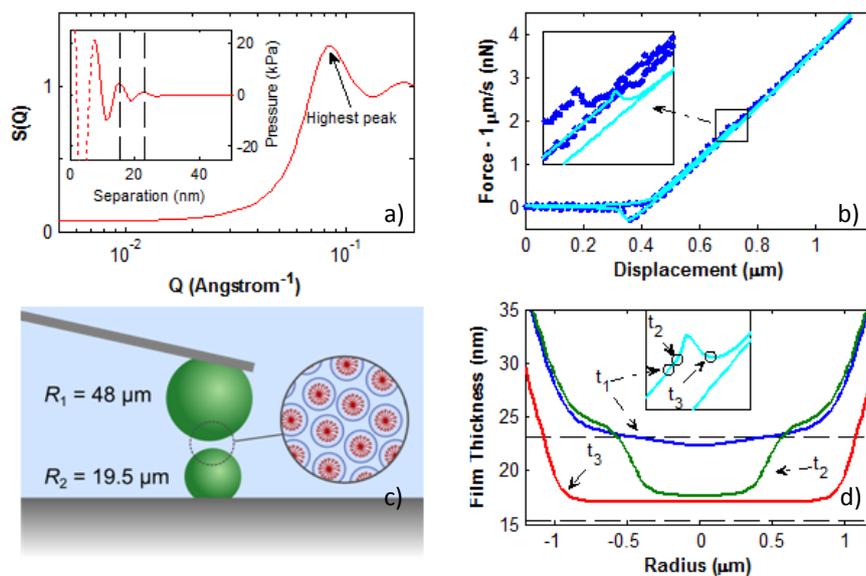


Figure a) Theoretically calculated structure factor (main figure) and structural disjoining pressure (inset); b) Comparison of experimental (dots) and theoretical (solid line) structural force results obtained from AFM; c) Schematic of the experimental system; d) The film profiles corresponding to the force jump in the inset of b)

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Probing Interactions between Colloidal Wood Extractives and Model Surfaces with Atomic Force Microscopy

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This paper reports the results of a study of the forces of interaction between colloidal wood extractives and model surfaces using atomic force microscopy (AFM). This required the development of a new method to attach colloidal particles to hydrophobically functionalised AFM cantilevers *in situ* in an aqueous environment. The colloidal particles were either natural wood extractive colloids or model compounds (oleic acid, abietic acid and triolein) colloids (Figure). Experiments measuring the interaction forces between these colloidal probes and cellulose, chromium and glass surfaces were carried out to understand why resin acids (from wood extractives) were found to be the major component desorbed from the surface of the newsprint paper to chromium surfaces during the printing process. It was found that triolein colloids have the greatest adhesion (8.1 mN m^{-1}) on a microcrystalline cellulose surface, a model for newsprint. The adhesion forces of abietic acid and wood extractives were strongest (about 3.7 mN m^{-1}) on a chromium surface, while the weakest interaction was recorded for oleic acid colloids (0.8 mN m^{-1}) on this surface. On a glass surface, the wood extractive colloids have the strongest adhesion force (7.0 mN m^{-1}), followed by triolein, abietic acid and oleic acid colloids. The results show that the oleic acid and triolein colloids have much greater adhesion to a cellulose surface than a chromium surface; whereas the adhesion of abietic acid colloids was similar on both surfaces. This may help explain the phenomena of predominant adsorption of resin acids onto chromium surfaces, almost to the exclusion of fatty acids and triglycerides.

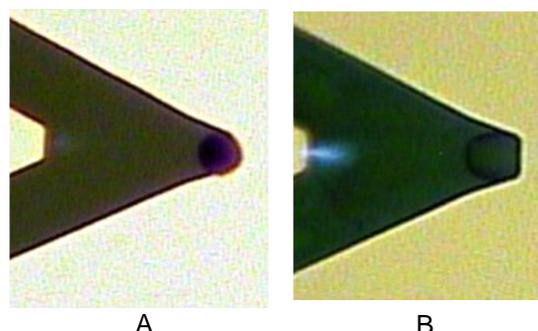


Figure 1 Abietic acid colloid attached to the functionalised cantilever (A); Oleic acid, triolein or wood extractive colloids attached to the functionalised cantilever (B)

OC083

Title TBC

Nick Ainger

Unilever Research and Development, Port Sunlight, UK

Abstract to follow

Understanding interfacial structure and diffusion in multilayer optoelectronic devicesIan Gentle¹, Paul Burn¹, Andrew Clulow¹, Paul Meredith¹, Michael James², Andrew Nelson²¹The University of Queensland, Brisbane, Qld, Australia, ²ANSTO, Sydney, NSW, Australia

Since the discovery that small fluorescent compounds and conjugated polymers could be used as the active material in organic light emitting diodes (OLEDs) about twenty years ago, intensive research has seen them move from relatively short-lived and inefficient devices to components of commercially available appliances. This research has prompted the development of other organic devices such as organic photovoltaic devices (OPVs), field-effect transistors (OFETs) and sensors. A fundamental feature of these devices is that they rely on electron transfer between layers of organic materials, which imposes certain requirements on the materials and the way they interact. For example, a high efficiency phosphorescent small molecule OLED will be typically comprised of four organic layers and five materials: two electron transport/hole blocking layers, a blended light-emitting layer and a hole transport layer. The interactions between these layers, particularly at elevated temperatures, are very important for device performance and durability.

Our group has been studying the morphologies of model devices based on the architectures of OLEDs, bulk heterojunction OPVs and fluorescent sensors for explosives using time-resolved neutron reflectometry. Examples of the outcomes of the work are (i) studies of OLED architectures which revealed that rapid interdiffusion occurs between the emissive layer and electron transport layer when heated above a critical temperature^{1,2}, (ii) studies of organic photovoltaic solar cells fabricated by sequential deposition that showed how interdiffusion between donor (P3HT) and acceptor (PCBM) layers leads to a bulk heterojunction structure³, and (iii) studies of sensors which revealed that the analyte diffuses reversibly throughout the active layer with accompanying swelling that depends on the structure of the sensing material^{4,5}.

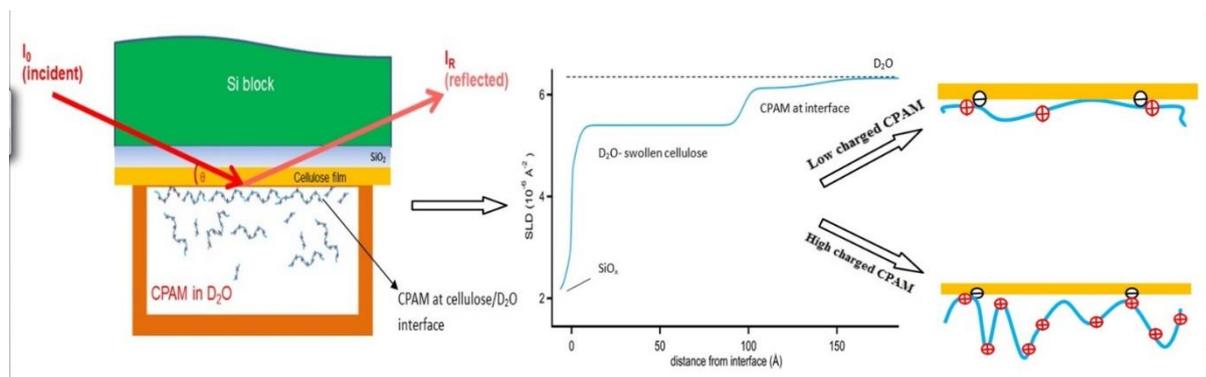
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Adsorption of cationic polyacrylamide at the cellulose-liquid interface: a neutron-reflectometry study

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The layer thickness and density of high molecular weight cationic polyacrylamide (CPAM) adsorbed at the cellulose-water interface was quantified by neutron-reflectometry. The thickness of a full monolayer of CPAM of different charge densities, but constant molecular weight (13MD) adsorbed with or without NaCl (10^{-3} M) was studied. Thin cellulose films (40.2 ± 7.1 Å) of roughness better than 10 Å were produced by spin coating a cellulose acetate-acetone solution and regenerating by alkaline hydrolysis. Film smoothness was greatly improved by controlling the concentration of cellulose acetate (0.13 wt%) and the hydrolysis time in sodium methoxide. The adsorption thickness of CPAM 40% charge 13MD at the solid-D₂O interface is 42.8 ± 3.8 Å on cellulose and 13.5 ± 2.3 Å on silicon. The adsorption thickness is an order of magnitude smaller than the CPAM radius of gyration. At constant molecular weight, the thickness of the CPAM layer adsorbed on cellulose increases non-linearly with polymer charge density (10.5 ± 1.2 Å at 5%). Addition of 10^{-3} M NaCl decreased the thickness of CPAM layer already adsorbed on cellulose. However, the adsorption layer on cellulose of a CPAM solution equilibrated in 10^{-3} M NaCl is much thicker (89.5 ± 11.2 Å for 40% CPAM). For high molecular weight CPAMs adsorbed from solution under constant conditions, the adsorption layer can be varied by 1 order of magnitude via control of the variables affecting electrostatic intra- and inter-polymer chain interactions.



OC086

Organic Polymeric Nanogels for Topical Drug Delivery: Studies of Interactions with Skin Models by Neutron Reflectometry

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A series of different crosslinked NIPAM (N-isopropyl acrylamide) based nanogels have been synthesized with high dilution free radical polymerisation. The Zetasizer results show that all the nanogels have a size in the nanometer range, which indicates their suitability in applications for topical drug delivery.

The morphology change of nanogels with temperature and the effect of hydrophobicity on their behavior were studied by Neutron Reflectometry equipped with Nima Trough. The surface activity increases with the increase in monomer and temperature, and this demonstrates the change in morphology of the nanogels. It is also suggested that the change of the nanogels with temperature is reversible when the percentage of crosslinker is no more than 30.

The penetration of nanogels through the ceramide lipid monolayer and multibilayers and the effect of the hydrophobicity on their penetration were then investigated by Neutron Reflectometry. The data shows that only the nanogels with 30% crosslinker can penetrate the ceramide lipid monolayer. Nanogel particles are deformed by the interaction and cooperated with lipid molecules. The interactions are not entirely reversible. In order to mimic the real skin, lipid multibilayers were obtained with the method of spin coating. The reflectivity data indicates that the nanogels with 30% crosslinker shows best penetration, followed by ones with 20% crosslinker, and the ones with 10% does not penetrate the multilayers. It can be inferred that the balance between hydrophobicity and hydrophilicity is important for nanogels to penetrate the lipid layers. Nanogels with 20%-30% crosslinker have the best performance.

In order to mimic the real skin, the mixture of Ceramide/Cholesterol/Fatty Acid was used to form the multi-bilayers. The penetration of nanogels into this multi-bilayers was performed at 35°C which is close to the physiological temperature of human body. The effect of enhancer Benzyl Alcohol on the penetration was investigated. It is shown that the ability of nanogels penetration of mixed lipid multi-bilayers is similar to that of ceramide lipid multi-bilayers: 30% crosslinked > 20% crosslinked > 10% crosslinked. Enhancer can help nanogels penetrate the lipid layers and its effect is time dependent

OC087

The Laminar, Transitional and Turbulent Open Channel Flow of Concentrated Suspensions

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Previous studies have shown that the free surface flow behaviour and characterisation of paste and thickened tailings material is of critical importance at discharge. Progress has been made utilising a bulk shear rate approach, and it has been demonstrated that this approach can be scaled for engineering design purposes in a manner similar to the approach of Metzner and Reed for tube flow. However, many unresolved issues remain for the flow behaviour analyses of paste and thickened tailings material in open channel flow. Arguably, the most acute of these are the application to viscoplastic paste material and the role that the yield stress may play in the concomitant location and description of the Laminar/Turbulent transition region. A further somewhat puzzling feature is that the turbulent flow regions for each slope assume a negative gradient after the laminar/turbulent transition. The wall shear stress values applicable to each bulk shear rate value are consequently non-unique. This would appear to be counter-intuitive, and requires further investigation. The objective of this paper is to develop and evaluate the open channel flow approach for the flow behaviour in the transition and turbulent region for viscoplastic flows of paste and thickened tailings material.

Transportation of concentrated suspensions is increasingly encountered in industries and natural debris flows. A typical example, where the terrain allows, is the transportation of thickened mining tailings from the thickening plant to the tailings disposal area through open channels. However, in comparison to pipe flow, the flow of thickened tailings which exhibits non-Newtonian behaviour through open channels has not received sufficient attention in the literature. This paper presents newly developed models to predict the flow behaviour in the laminar and the turbulent regimes through open channels. The objective of these models is to accurately evaluate the frictional forces caused by the material's non-Newtonian viscous behaviour at the flow boundaries.

The flow behaviour predictions of these semi-theoretical models are discussed and validated using previously published experimental data. The results show that the new models provide improved estimates of the friction at the boundary; and average velocity predictions obtained by the new models are more consistent with the experimental data for Kaolin and Bentonite suspensions.

OC088

Dynamic light scattering and method divergence

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With a history dating back more than 40 years, dynamic light scattering (DLS) continues to be one of the most routinely applied methods for particle size analysis due to its ease of use and prevalence. Despite this, it appears that there is still much to be learnt about interpreting DLS results, and understanding how they relate to particle size measurements performed with other methods. In this work, we report on our results from recent international comparisons on nanoparticle size, in which measurements by metrology institutes from around the world were made on the same set of materials employing a host of techniques including DLS, atomic force microscopy and electron microscopy. We review the observed method divergence which is particularly pronounced between intensity-based hydrodynamic particle size distributions measured by DLS and number-based distributions measured using microscopy techniques. We illustrate how this divergence is being addressed by applying a number of different corrections. Such corrections include corrections to convert intensity-based to number-based distributions; corrections for the angular and concentration dependence; and correcting for the hydration layer associated with particles. For some samples, the magnitude of these corrections can be very significant and exceed 30 %. The validity, applicability and implications of such corrections are discussed.

OC089

Influence of extreme temperatures and pressure on the rheology and colloidal properties of mineral suspensions for applications in drilling for deep earth resources

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The world's energy resources are becoming more difficult to extract from underground, and access to deep earth resources such as geothermal energy subjects aqueous fluids to extremes in temperature and pressure (up to 100 MPa and 300 °C). Such conditions can render conventional drilling, fracturing and cementing fluids ineffective. Fluid properties are poorly characterised at these conditions, making fluid behaviour unpredictable and largely uncontrolled; we seek to rectify this so that we can facilitate improved design.

Drilling fluids typically have a composition to position them on the boundary between solid-like and liquid-like behaviour. Operating at this boundary makes their behaviour sensitive to changes in fluid ionic strength, pH, solids content, and most importantly for geothermal drilling operations, temperature. Changes in these conditions can alter their yield stress and high-shear viscosity. Measurement techniques to accurately characterise their rheology are vital, as is an understanding on the colloidal properties leading to them. Here we report the challenges associated with characterising aqueous mineral suspensions under extremely high temperature (up to 300°C) due to the instrument design constraints associated with the high pressures required to maintain the liquid state. Prediction of drilling fluids behaviour at *in situ* conditions requires considered use of multiple geometries to ensure that rheological characterisation is robust and not subject to confounding measurement errors. We demonstrate appropriate methodologies and use these to show how increasing temperature causes a dramatic increase in the yield stress of aqueous Hausmannite suspensions.

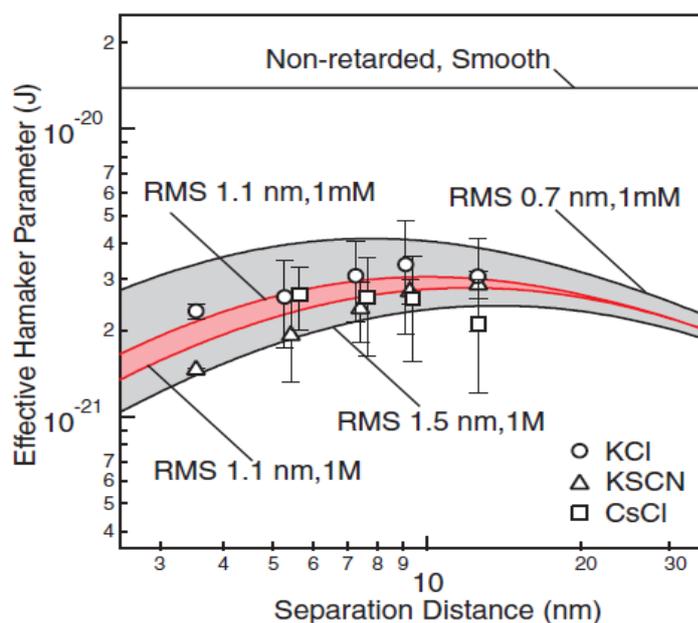
Reduced Effective Dispersion Interactions Between Rough Surfaces

Mihail Popescu

Max Planck Institute for Intelligent Systems, Stuttgart, Germany

Colloidal probe AFM investigations of the interactions between carboxylate colloidal latex particles of about 2 μm in diameter immersed in aqueous solutions of monovalent salts, with systematically varied ionic strength, type of salt, and solution pH (surface charge densities of the particles), allowed accurate determination of the dispersion forces acting between the particles.¹ The measured force profiles (force vs separation distance) can be quantitatively interpreted within the classic DLVO theory.² The Hamaker constant thus estimated is $(2.0 \pm 0.5) \times 10^{-21}$ J at a separation distance of about 10 nm, which reveals that the measured dispersion forces are significantly weaker than the ones expected from the Lifshitz theory for smooth surfaces.³ Moreover, this apparent Hamaker constant is basically independent of the salt concentration (as well as of the type of salt).

We show that these results can be rationalized and quantitatively explained by accounting for the roughness of the surfaces (separately determined by using AFM imaging) via a mean-field statistical averaging of the Lifshitz interaction appropriately weighted by the roughness distribution. It is concluded that the combination of retardation and roughness effects substantially reduces the effective Hamaker parameter from the value expected for smooth surfaces and suppresses the ionic strength dependence of the dispersion forces.¹ As shown in the figure, the theoretical predictions are in full agreement with experiment.



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OC091

Successful continuum solvent model of ionic interactions with the air water interface

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The explanation and prediction of the interaction of ions with the air–water interface has been a central challenge of physical chemistry for over a century. Renewed focus on this problem in recent years has been driven by the surprising observation that large halide anions adsorb to the air–water interface.^{1,2}

In essence this problem amounts to calculating the change in the solvation energy of an ion as it approaches the interface. We have previously³ developed a satisfactory continuum solvent model of ionic solvation energies in the bulk. Here,⁴ we generalize this model to calculate the free energy change as an ion approaches the air–water interface. We use the COSMO method, which treats the ions quantum mechanically and includes the change in the Born energy and the polarization response of the ion. Approximate expressions for the dispersion repulsion, cavity attraction and surface potential contributions are also included. This model reproduces the ion specific behaviour of the surface tensions of electrolyte solutions and is in agreement with *ab initio* molecular dynamic simulation of the iodide anion at the interface.⁵ The model provides a straightforward physical explanation of iodide's adsorption. No ion specific fitted parameters are necessary and all of the important contributions to the interactions are included.

Solving this problem is directly important for atmospheric chemistry and for understanding the properties and interactions of bubbles and nanobubbles. In addition to this, the model is also important as a prerequisite to understanding the more complex interactions of ions with protein and mineral surfaces. Our model is conceptually simple and has low computational demand. This facilitates further extensions to these systems, which are important in biology, medicine and industry.

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Interfacial and Near Surface Nanostructure in Soft Matter SystemsRob Atkin¹, Aaron Elbourne¹, Greg Warr², Kislou Voitchovsky³¹University of Newcastle, Newcastle, NSW, Australia, ²University of Sydney, Sydney, NSW, Australia, ³Durham University, Durham, UK

A unique, but unifying, feature of ionic liquids (ILs) is that they are nanostructured on the length scale of the ions; in many ILs well-defined polar and apolar domains exist and may percolate through the liquid. Near a surface the isotropic symmetry of the bulk structure is broken, resulting in different nanostructures which, until now, have only been studied indirectly. *In situ* amplitude modulated atomic force microscopy has been used to resolve the 3-dimensional nanostructure of *protic* ILs and *solvate* ILs at and near the surfaces of mica and graphite. The surface and near surface structures are distinct and remarkably well-defined (c.f. Figure 1), but are very different from previously accepted descriptions. Interfacial nanostructure is strongly influenced by the registry between cations and the substrate, whereas near surface nanostructure is sensitive to both cation and anion structure. The results obtained for the ILs are compared to those of aqueous surfactant sponge phases. The sponge phase nanostructures are similar except that the features have length scales an order of magnitude larger. Together, these results reveal how interfacial nanostructure in soft matter systems can be tuned through ion structure, informing “bottom-up” design and optimisation of ILs for diverse technologies including heterogeneous catalysis, lubrication, electrochemical processes, and nanofluids.

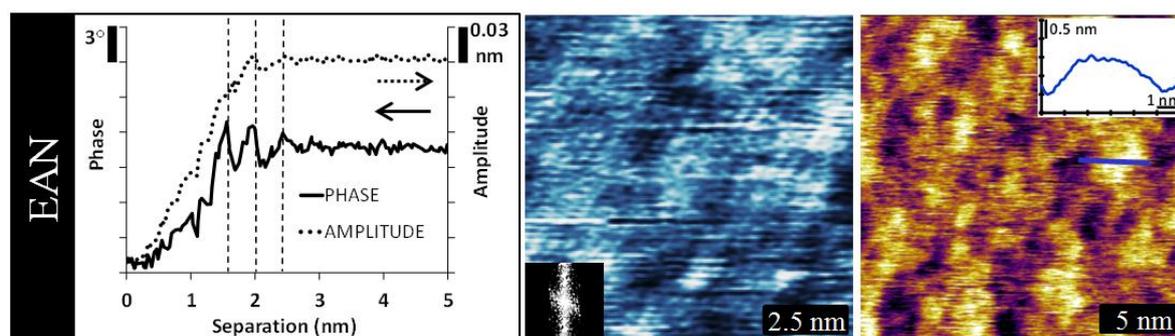


Figure 1. *In situ* amplitude modulated atomic force microscopy force spectroscopy and images of the surface adsorbed ion layer and near surface layer at the ethylammonium nitrate – mica interface.

Hydrophobicity Modulated Specific Anion Effects on Weak Polycationic Brushes

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Many physicochemical phenomena such as polymer solubility and ion-partitioning at interfaces are dependent on the identity of the ion. These specific ion effects are typically framed by the Hofmeister series with kosmotropic (water structure making) and chaotropic (water structure breaking) ions at either end. Traditional explanations in terms of the ion's effect on the structure of water have been shown to be inadequate, but remain useful labels for comparison. A full explanation must include interactions between solvent, solute and ion.

Responsive polymer brushes are end-grafted chains which respond to changes in environment. We have previously demonstrated the pH and salt response of a poly(2-(diethylamino)ethyl methacrylate) (PDEA) brush as a function of potassium nitrate concentration¹. The brush swelled rapidly over a narrow concentration range in the osmotic brush regime (low salt), while theory predicts a gradual increase. We proposed that this is due to competition between hydrophobic polymer-polymer interactions and the osmotic pressure of counterions in the brush. Recent work probes this effect through the use of dimethyl- (PDMA) and diisopropyl- (PDPA) analogues of PDEA which provide a range of hydrophobicity (PDPA > PDEA > PDMA). Specific ion effects were also studied by including the potassium salts of acetate (strongly kosmotropic), nitrate (mildly chaotropic) and thiocyanate (strongly chaotropic). To our knowledge, this presents the first study of specific anion effects on weak polyelectrolyte brushes.

The salt and pH reponse of the brushes was studied using ellipsometry (Figure 1) and quartz crystal microbalance. Specific ion effects are prominent at high salt concentrations (salted brush) where chaotropes, which are better able to partition themselves within the brush, result in collapse while no collapse is observed for the kosmotropic acetate. The effect of monomer hydrophobicity is most apparent at low salt concentrations where PDPA and PDEA swell with increasing salt concentration for nitrate and acetate, while the hydrophilic PDMA is swollen even at 0.1 mM. Interestingly, PDPA (most hydrophobic) doesn't appear to swell in thiocyanate (most chaotropic) at any concentration.

(1) Willott, J.D.; Murdoch, T.J.; Humphreys, B.A.; Edmondson, S.; Webber, G.B.; Wanless, E.J. *Langmuir*, **2014**, *30*, 1827-1836

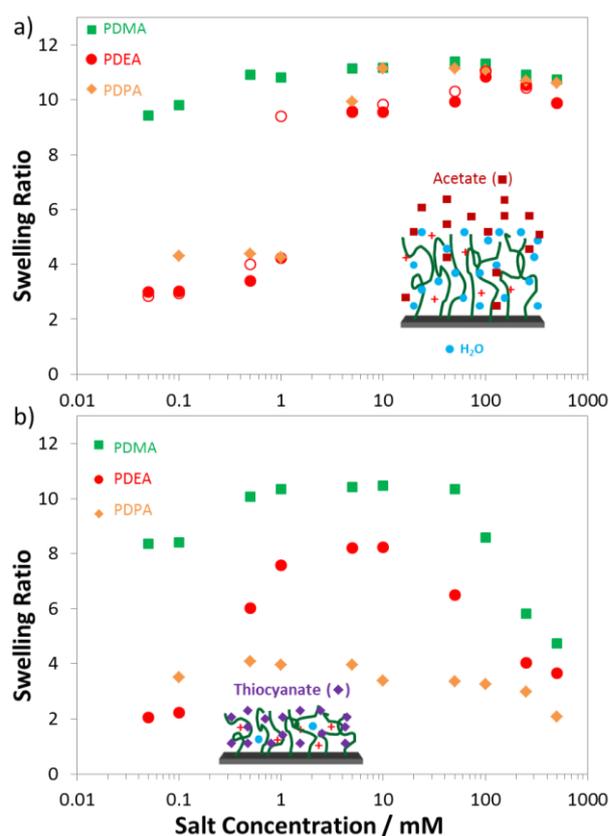


Figure 1 – Swelling ratio (swollen thickness/dry thickness) as a function of salt concentration determined by ellipsometry for a) potassium acetate and b) potassium thiocyanate

Preparation of Multiwall Carbon Nanotubes (MWCNTs) stabilised by highly branched hydrocarbon surfactants and dispersed in Natural Rubber Latex nanocomposites

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The performance of single-, double-, and triple-chain anionic sulphosuccinate surfactants for dispersing multiwall carbon nanotubes (MWCNTs) in natural rubber latex (NR-latex) was studied using a range of techniques, including field-emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), and Raman spectroscopy. The conductivities of the nanocomposites were also investigated using four-point probe measurements. Here, MWCNTs were efficiently dispersed in NR-latex with the aid of hyper branched tri-chain sulphosuccinate anionic surfactants, specifically, sodium 1,4-bis(neopentyloxy)-3-(neopentyloxycarbonyl)-1,4-dioxobutane-2-sulphonate (TC14). This paper highlights that TC14 performs much better than that of the commercially available surfactant sodium dodecyl sulphate (SDS), demonstrating how careful consideration of surfactant architecture leads to improved dispersibility of MWCNTs in NR-latex. The results should be of significant interest for improving nanowiring applications suitable for aerospace-based technology.

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The pH and salt responsive behaviour of a weak polybasic brush

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Surface-anchoring of stimulus responsive polymer brushes offers a route to preparing novel functional surfaces. By selecting the appropriate monomer functional group, brushes can be polymerised directly from initiator groups tethered to the interface, and respond to a wide range of environmental stimuli (pH, temperature and ionic strength). In this way the physicochemical properties of a surface can be tailored to an intended application. Our work¹ focuses on studying and understanding the fundamental response of weak polyelectrolyte brushes (i.e. brushes that contain ionisable repeating monomers). Specifically we have investigated the behaviour of weak tertiary amine methacrylate-based polybasic brushes, e.g. poly(2-(diethylamino)ethyl methacrylate), poly(DEA).

We have employed a suite of surface characterisation techniques including in-situ ellipsometry, quartz crystal microbalance (QCM), atomic force microscopy (AFM) and most recently neutron reflectivity to gain an insight into polyelectrolyte brush behaviour. The pH-response of poly(DEA) brushes is hysteretic in nature and brush swelling occurs faster than brush collapse. This is attributed to the formation of a hydrophobic skin that retards the egress of solvent from the brush upon deprotonation of the polymer, see Figure 1a and b. Poly(DEA) brushes are not only pH-responsive but they also display interesting non-monotonic ionic strength dependent behaviour, collapsing at low and high salt concentrations, furthermore this response has been found to be anion-specific with the behaviour following the Hofmeister series, Figure 1c and d.

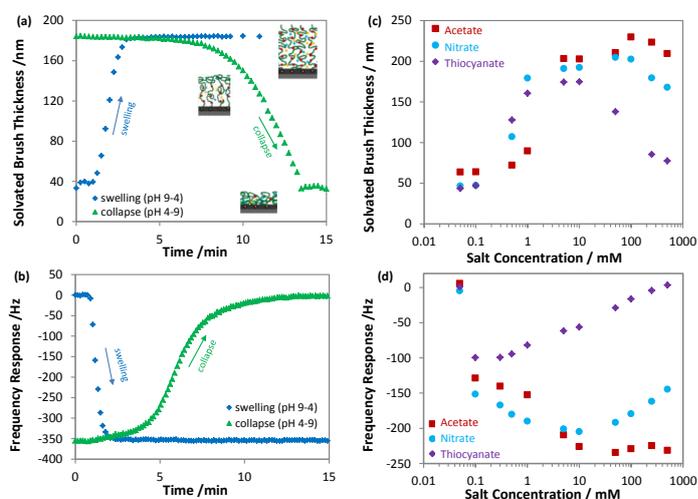


Figure 1.

(a) Kinetics of the pH-induced swelling and collapse for a poly(DEA) brush as measured by ellipsometric solvated brush thickness

(b) QCM frequency response of poly(DEA) brush upon pH-induced swelling and collapse

(c) Equilibrium brush thickness (measured by ellipsometry) as a function of salt concentration for 3 Hofmeister series anions

(d) Equilibrium QCM frequency response as a function of the concentration of different Hofmeister series anions

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OC097

Force measurement between emulsified oil drops in presence of mixed surfactant system (Ionic/Non-Ionic)

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The stability of emulsions plays a crucial role in formulation of many food, detergent, pharmaceutical and personal care products. Most of emulsion formulations are stabilized by mixed surfactant system containing a combination of ionic and non-ionic surfactants. There have been many experimental and theoretical works in literature that studied adsorption of mixed surfactants onto air-water interface. However, it is the adsorption of mixed surfactants onto oil-water interface that is relevant to many practical applications. Hence, we experimentally studied the interaction forces between oil drops coated with surfactant mixtures. Also, many of the experimental and theoretical studies existing in literature mainly focus on mixed surfactant system containing ionic surfactants such as n-alkyl-sulfates ($C_nH_{2n+1}SO_4Na$); hence they are well studied. However, there are very few experimental studies on mixed surfactant systems involving n-alkyl-sulfonates ($C_nH_{2n+1}SO_3Na$). It is known from few existing experimental studies in literature that n-alkyl-sulfonates show striking differences compared to n-alkyl-sulfates, when mixed with other surfactant even though most of the physical properties of sulphate and sulfonate are similar. Therefore, to bridge the gap in the exiting literature on n-alkyl-sulfonates adsorption at oil-water interface, in our study, we used sodium 1-octanesulfonate monohydrate (C_8), ($C_8H_{17}SO_3Na.H_2O$) as an ionic surfactant. We used pentaethylene glycol monododecyl ether ($C_{12}E_5$) as a non-ionic surfactant.

Using Atomic Force Microscope (AFM), we measured forces between colliding oil drops (n-Tetradecane) in presence of pure surfactants as well as mixture of surfactants in the range of pre-micellar compositions. Unlike, neutron scattering techniques which are used to probe charging behavior of micelles well above CMC (Critical Micelle Concentration), AFM is capable of probing the charging behavior of oil-water interface in pre-micellar composition range. The measured force-distance curves are analyzed using Chan-Dagastine-White model to extract the surface potential of the oil-water interface. In order to elucidate the effect of competing adsorption of surfactants onto oil-water interface, we measured adsorption isotherms of pure surfactants and mixture of surfactants by pendant drop method. We found that the adsorption of both the ionic (C_8) and non-ionic ($C_{12}E_5$) surfactants follows Frumkin model. The fitted model parameters from pure surfactant adsorption isotherms are used to predict isotherms of mixed surfactants at mixing ratios of 6:1 and 15:1. Surface excess calculations show that adsorption at oil-water interface is dominated by anionic surfactant due to its high diffusivity and adsorption rate constant. The surface charge density on oil-water interface obtained from theoretical surface excess calculations are compared with that calculated from surface potential and force measurements. Thus, AFM force measurement combined with adsorption isotherms offers a unique perspective on charging behavior and stability of oil in water emulsions in pre-micellar compositions of mixed surfactant system.

OC098

Depletion and oscillatory structural forces between drops and bubbles

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In complex fluids, soft or deformable components, such as drops, bubbles, or capsules, respond to their surrounds in a far more complicated manner than rigid particle dispersions. This creates challenges in the processing and the characterization of these systems for a diverse set of applications. These applications range from the purification of minerals or pharmaceuticals using solvent extraction processes, to the formulation of emulsions and foams in food and personal care products. Through a combination of novel experimental methods, mainly using Atomic Force Microscopy (AFM) to visualize the collisions between micro-drops or micro-bubbles on the nanoscale, coupled with theoretical models, we have been able to quantitatively link the dynamic coupling of shape changes with external forces that control their behavior for a range of systems involving drops and bubbles.

This talk will focus on how oil-water and air-water deformable interfaces are mediated by the presence of highly concentrated surfactant systems or non-adsorbing poly-electrolytes. We observe significant differences between the structural forces between these deformable interfaces compared to the periodic oscillatory structural forces commonly observed between rigid interfaces. In addition, quantitative comparison between these system types indicates that the deformable nature of droplets allows them to act as far more sensitive probes than solid spheres. Furthermore, the responsive nature of soft surfaces can give rise to unexpected behavior not encountered in rigid systems including reversible aggregation/flocculation for emulsion droplets and, potentially, spatial ordering within concentrated emulsion phases. The impact of hydrodynamic drainage effects on the resulting force behavior as well as changes associated with the aspect ratio of the nano-colloid will also be discussed.

Ligand-mediated Interactions between Nanoscale Surfaces Depend Sensitively and Non-linearly on Temperature, Facet Dimensions, and Ligand Coverage

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Nanoparticles are often covered in ligand monolayers, which can undergo a temperature-dependent order-disorder transition in solution that switches the particle-particle interaction from repulsive to attractive [1]. In this work we look at how changes in the ligand surface cover and facet dimensions, going from the macroscale to the nanoscale, affect the ordering of the ligand and solvent molecules and the interaction between the ligand monolayers. In particular, we consider the case of strongly bound octadecyl ligands on the (100) facet of CdS in the presence of an explicit *n*-hexane solvent (Fig. 1a).

Depending on the facet dimensions and surface cover, we observe three distinct ordered states that differ in how the ligands are packed together (Fig. 1b) and which affect the thickness of the ligand shell and the structure of the ligand-solvent interface. The temperature-dependence of the order-disorder transition also changes substantially, broadening and shifting to lower temperature in a non-linear manner as the nanoscale is approached. Significantly, we find that ligands on nanoscale facets can behave very similar to those on macroscopic surfaces, and that some facet dimensions affect the ligand alignment more strongly than others.

As the ligands order, the interaction between the monolayers becomes attractive, even well below full cover (Fig. 1c). The strength of attraction is strongly affected by the ligand cover, when compared at constant temperature, but only weakly by the facet width, when normalized by facet area. These changes will influence whether ligand-covered particles remain suspended in solution, randomly aggregate, or undergo controlled assembly into large-scale ordered structures.

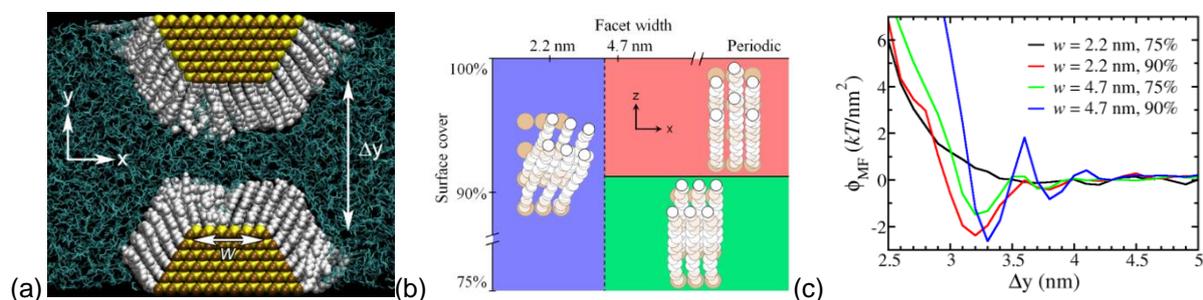


Fig. 1. (a) Octadecyl ligands order on two CdS(100) surfaces in *n*-hexane at 290 K. The facet width w and surface cover strongly affect (b) the structure of the ordered state and (c) how the surfaces interact with one another (ϕ_{MF} is the potential of mean force normalised by the facet area).

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Surface Charge and Biphasic Events in Tunable Resistive Pulse Sensing

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This presentation will discuss development of colloidal surface charge measurement techniques using tunable resistive pulse sensing (TRPS).^{1,2} In TRPS, a particle moving through a pore in a thin membrane momentarily blocks the ionic current passing through the pore. The resulting resistive pulse can yield information regarding particle concentration and size, as well as charge. An experimental comparison of TRPS with dynamic light scattering (DLS) will be presented. Key variables that have been probed include electrolyte composition and particle surface chemistry, with the latter quantified using titration measurements at manufacture. Although there are existing theoretical links between surface chemistry and electrophoretic mobility (usually quantified using the zeta-potential), improved experimental understanding is needed for applications. Efficient assessment of surface charge is important for emerging technologies in nanomedicine, environmental science and the food and beverage industry. Knowledge of surface charge can assist with (for example) analysis, diagnosis, quality control, or regulatory compliance.

One particularly interesting aspect of this work is the appearance of biphasic pulses, which exhibit both conductive and resistive components. This effect has recently been reported for similar pores and explained using a concentration polarization mechanism.^{3,4} We will discuss the conditions under which biphasic pulses are observed in TRPS, and variations with experimental variables such as pore size, applied pressure and applied potential (see Figure).

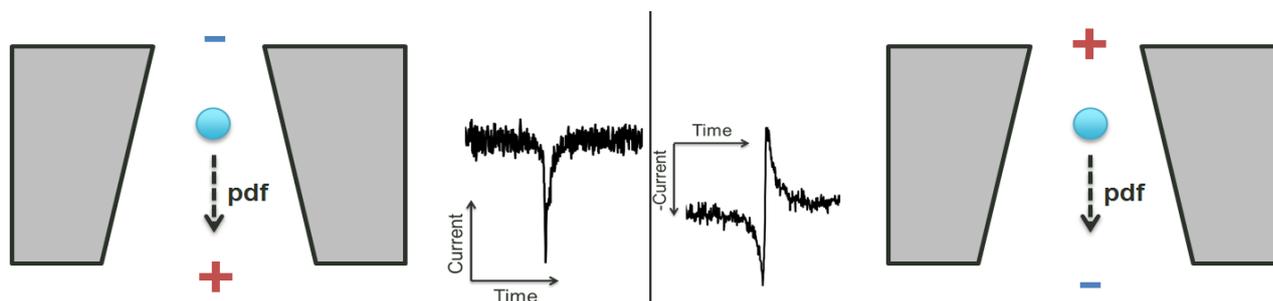


Figure: Experimental pulses for polystyrene spheres in 10 mM salt are entirely resistive when the particle moves towards a positive electrode (left), but biphasic when the potential polarity is reversed (right). Schematic diagrams show cross-sections through conical pores, with the polarity of the applied potential and the direction of pressure-driven flow (pdf) indicated.

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Tunable nanophotonics

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Tailored surfaces exhibit optical properties which differ from those from bulk materials. One of them is the localized surface plasmon resonance, which becomes apparent when an external electromagnetic field incident on metal elements (metal nanoparticles or nanovoids, for instance) induces electron cloud delocalization. Net charge difference on surfaces acts as restoring-force producing dipolar oscillation. Optical response is originated from the strong localized metal absorption when the frequency of the electromagnetic field becomes resonant with the coherent electron motion. One interesting issue concerning the photonics of surfaces is the optical properties modulation through external inputs. In this context, merging of metal and smart-soft-polymer technologies to make hybrid systems leads to successful results. In this talk, a set of three hybrid systems are presented, pointing out their main properties and applications. 1) Gap controlled 2D metal particle arrays: a simple alternative to the classical ensembles based on the control of the electrostatic and interfacial forces [1]. We use tuneable mechanical spacers (responsive polymers) located in between the particles, being the particle gap set by the swelling state [2]. The use of Au@PNiPAM core-shell nanoparticles achieves high precision and continuous interparticle-gap tuning [3]. 2) Tunable optical surfaces based on soft particles photonic nanovoids. 3) Tunable optical surfaces based on soft hybrid-particles photonic nanovoids.

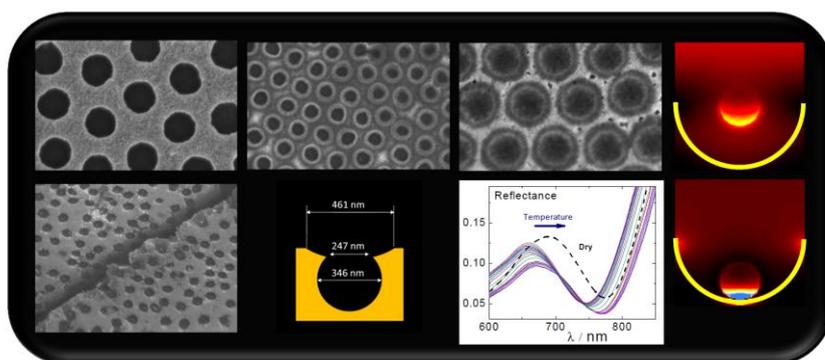


Figure 1. Tunable optical response from hybrid nanovoids

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Differential Dynamic Microscopy: a New Technique for Measuring Dynamics in Colloids and Soft Matter.

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The dynamics of particles suspended in a solvent are of broad interest, from the dynamics of colloidal fluids, glasses and gels, to the study of chemotaxis, disease propagation and biofilm development in bacteria, to the characterization of microorganism motility.

The two most widely used techniques for studying such systems are Dynamic Light Scattering (DLS) and Microscopic Tracking, which each have advantages and disadvantages: DLS is a well established technique for particle sizing and investigation of colloidal systems^{1,2}, and provides excellent ensemble averages, but is limited to scattering angles greater than $\sim 15^\circ$ (corresponding to length scales less than $\sim 3 \mu\text{m}$), which limits the length scales which can be probed; Tracking on the other hand is limited to objects of size micrometres or greater, and as only a finite number of objects can be tracked, making genuine ensemble averaged measurements is time consuming and difficult.

A new technique with great potential in this area is differential dynamic microscopy (DDM)^{3,4}. It uses a white light microscope and involves imaging a time-evolving sample at fast frame rates, and measuring the intensity fluctuations in each pixel. Fast Fourier transformation (FFT) of the difference between images enables extraction of dynamics in reciprocal space, like DLS. However, DDM accesses larger length scales ($\sim 10 \mu\text{m}$ or more), allowing, for example, studies of motile bacteria^{5,6}. Moreover, it works under a variety of sample conditions and imaging techniques^{7,8}. In this paper we will explain the principle of the technique (see figure 1), and illustrate with results on colloidal suspensions and motile bacteria. We investigate the effects of multiple scattering, and show how this technique provides reliable data under conditions where DLS fails. We will briefly discuss the broader applications of the technique in colloids and soft matter.

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OC103

Electrokinetic Instabilities in Multiphase Microfluidic Flows

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Multiphase flows in micro- and nano-scale devices are particularly useful for many biological and biochemical processes. In some types of microfluidic devices, stability of the interface between phases is crucial in order to keep the phases separate so that adequate amounts of reactants are available for a reaction or process to occur. In other types of devices, it is necessary to destabilise interfaces in order to mix phases to initiate a reaction if the phases are miscible, or to form emulsions or drops if the phases are immiscible. The use of electric fields to drive and manipulate flow is common, and the presence of free charge in aqueous solutions is significant.

Here we utilise a numerical model previously developed that is capable of capturing diffuse regions of charge within a conducting phase [1], and also capable of modelling charge on the interface between phases [2]. The model is applied to two common microfluidic multiphase scenarios: i) a planar aqueous/solvent interface exposed to an external electric field, and ii) an aqueous drop immersed in a solvent, also in the presence of an external electric field. The effects on the interfacial stability of charge present in the conducting phase and at the aqueous/solvent interface are characterised.

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Multi-scale lubrication of multiphase complex fluids

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Lubrication in real life environment is often associated with lubricants that contain particulates. Food products during oral processing, cosmetic and oral care products during in-use application, as well as plant mucilages that aid root penetration through tough soils rely on several lubrication mechanisms to effectively minimise energy losses associated with friction. Many such complex fluids contain particulates, which may facilitate lubrication in some cases, while in others cause numerous challenges including excessive wear and loss of lubricity. In this report we examine the behaviour of suspensions confined between compliant, rough rubbing surfaces, which mimic lubrication in biological systems and food/personal care applications. Firstly, we investigate the lubrication of microsphere suspensions, and probe the influence of matrix viscosity, particle phase volume, surface roughness and wetting, and slide-to-roll ratio (SRR). In general, the suspensions behave as a continuum in the elastohydrodynamic regime provided the film thickness, which is predicted from the speed-viscosity, is greater than the particle diameter. Below this, the system transforms to the mixed regime that is defined by the matrix viscosity. Entrainment at narrow gaps is made possible by substrate deformation whereby friction in the boundary regime is governed by particle rolling that is independent of SRR and phase volume of particle above 5%. Secondly, we investigate lubrication of starch suspensions in binary mixtures of ionic liquid, 1-ethyl-3-methylimidazolium acetate (EMIMAc), and water. We show that for the mass ratio of ionic liquid below 0.6, the lubrication behaviour is dominated by starch particles, qualitatively similar to the behaviour of model suspensions. However for the ratios ≥ 0.6 , a critical transition in the solvent quality of the IL-water mixtures results in partial leaching of starch material into solution. It was found that the soluble starch-based polymers are capable of adsorbing on hydrophobic PDMS surfaces. This adsorption causes the reduction in friction up to 4 times compared to a pure solvent. Moreover it was found that for these systems the friction behaviour is independent of particle phase volume. These results are interpreted in favour of a mechanism whereby particle entrainment is controlled by a force balance in a wedge-shaped inlet formed between two rubbing surfaces. In this scenario, the particle entrainment relies on the friction force between the particle and the surface to be greater than the mechanical force associated with surface deformation. Adsorption of polymers results in surface modification that reduces friction between particles and the surface, which results in abolition of particle entrainment. This study provides a benchmark for biotribological studies into more complex particle systems common in plant systems, and consumer products.

OC105

Structure and Forces in Self-Supported Foam Films

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Self-supported foam films are usually in a liquid state. In foam films two surfaces come in close proximity. The stability of foam films is remarkable due to the enormous surface area formed while usually formation of large surface areas is avoided in nature if possible. In order to keep the foam film metastable, i.e. achieving lifetimes of a few hours or more, surfactants are added to the solution forming the foam film. In some cases the presence of inorganic salts seems to be helpful in order to keep the foam film stable. Electrostatic and van-der-Waals forces are used to describe the thickness and structure of foam film. [1] However, little is known about the internal structure of foam films: the coverage of the surface with surfactant and solute, the orientation of the molecules at the surface, and location of the charges. Such information is required to give reasoning for the models used to describe foam films. By measuring directly concentration depth profiles at the surface of foam films, the above listed quantities describing the structure of foam films can be determined. [2] The technique used to measure the concentration depth profiles is neutral impact collision ion scattering spectroscopy (NICISS).

In this presentation the techniques for measuring concentration depth profiles of foam films will be shown and results of foam films stabilised by ionic and non-ionic surfactants discussed. We will show examples of foam films stabilised by the ionic surfactants hexadecyltrimethylammonium bromide (C16TAB) and the non-ionic surfactant dodecyldimethyl phosphineoxide (C12DMPO). In the latter case also ion specific effects have been investigated by adding various sodium halide salts over a range of concentrations. The anions show differences in their propensity to adsorb at the surface.

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The Impact of Surface Roughness on Surface Forces

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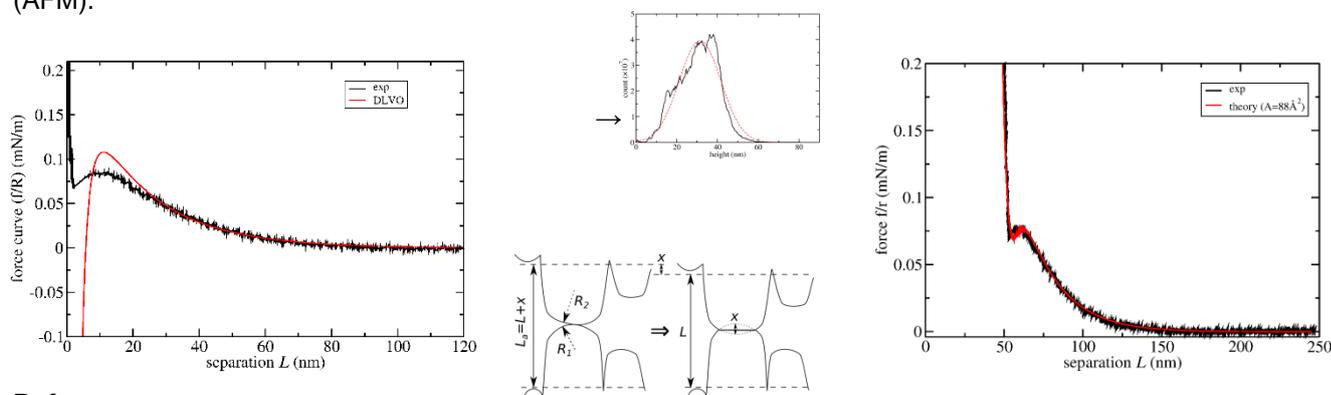
The classic DLVO theory commonly employed to interpret surface force measurements treats the surfaces as ideal, smooth interfaces. But real surfaces have a degree of roughness, with root-mean-square deviations (RMS roughness σ) in the height of the surface reaching as high as 10 nm. This phenomenon confounds interpretation of the experimental data and may lead to incorrect estimates of surface potential and charge.

We present a new model which extends DLVO theory in two ways in order to account for surface roughness. Firstly, the noncontact DLVO force is averaged using a statistical description of surface roughness to obtain a “roughened” DLVO force. Secondly, a contact force is added, derived from the elastic compression of asperities in contact. The contact force is characterised by the radius of curvature of asperity tips.

The general impact of roughness on the noncontact force is to amplify short-range interactions, whether attractive or repulsive. The impact of elastic compression of asperities is to generate a repulsive contact wall, setting an “apparent zero” which is located at a position around 4σ out from “true zero”. The contact wall may be responsible for certain kinds of “hydration forces”, that is non-DLVO repulsion observed in some systems.

Analytic expressions are derived for the contact force and for an exponential non-contact force between surfaces with normal Gaussian roughness. The effect of non-Gaussian surface roughness may be treated using a histogram of surface heights measured by AFM, and can make a significant difference to the roughened forces.

The theory is tested on surface forces measured between titania surfaces by atomic force microscopy (AFM).



Reference

“Surface forces: Surface roughness in theory and experiment”

Parsons, D.F., Walsh, R.B., and Craig, V.S.J.

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OC107

Interaction Force between Silanated Silica Surfaces in Organic Solvents

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Colloidal particles dispersed in non-aqueous, organic solvents are used in many industrial products, such as paints, cosmetics, ceramics, and electronics. To obtain stable suspensions, it is important to understand in situ the interaction force between the colloidal particles in a solvent. Compared with the interactions in aqueous solution, those in organic solvents are still less well understood. In particular, a more fundamental understanding of the relationships between the surface properties of the particles and the interaction force is desired.

In the present study, we focused on the measuring the interaction force between silanated silica surfaces in organic solvents using an atomic force microscope (AFM) and investigated the relationship between the affinity of the solvent for the surface and the interaction forces. The interaction forces between silica surfaces modified with octadecyltrichlorosilane in ethanol/water mixtures showed a long-range attractive force when the ethanol ratio is less than 25%. Similar forces were seen in other water-soluble organic solvents. A possible origin of these long-range forces is the adsorption of the solvent molecules on the hydrophobic surfaces, which induces the attractive force.

High Density Monolayer of Metal Complex on Structurally-Defined Surface:

Preparation and Application in Catalysis

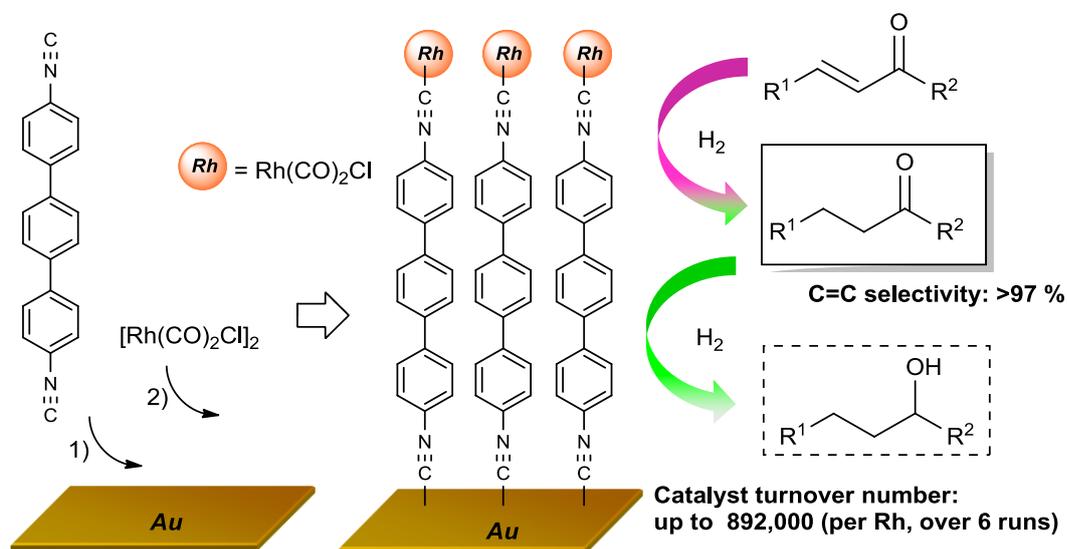
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Self-assembling of organic molecules on surface automatically forms ordered densely packed molecular monolayer. This spontaneous phenomenon can be used as one of the promising low-cost methods to prepare functional materials. One of the most commonly used systems is self-assembled monolayer of alkane thiolate on gold surface, whose application has been expanded to a wide range of functional devices including catalyst.^[1] We recently envisioned utilization of much less studied monolayers, monolayers of isocyanide, for catalyst preparation. We report herein the modification of gold surface with 4,4'-terphenylenediisocyanide (TPDI) as platforms for high turnover and selective Rh-catalyst in C=C hydrogenation of α,β -unsaturated carbonyl compounds.^[2]

A gold surface evaporated on glass plate was immersed in a CH_2Cl_2 solution of TPDI to obtain the monolayer of TPDI on Au surface. The successive immersion in a benzene solution of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ gave Rh-immobilized monolayers, **[Au]-TPDI-Rh**. Characterization of thus obtained surfaces was conducted by XPS, IR-RAS and ICP-MS.

The test reactions with 2-cyclohexene-1-one showed that **[Au]-TPDI-Rh** exhibits high selectivity to cyclohexanone over further reduced product, cyclohexanol. The selective C=C hydrogenation with **[Au]-TPDI-Rh** could be applied to a wide variety of α,β -unsaturated carbonyl compounds. Typical catalyst turnover numbers are as high as in a range of 50,000 to 150,000 per Rh atom grafted on the monolayer. The catalyst can be used repeatedly at least five times without obvious deactivation. The monolayer of diisocyanide molecule on gold surface was thus confirmed as a useful platform for selective Rh-catalyzed hydrogenation reaction of α,β -unsaturated carbonyl compounds.^[2]



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Influence of Surface Heterogeneity, Water Concentration, and Humidity on the Surface Diffusion of [Rmim][NTf₂] Precursor Films on Mica

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Ionic liquids (ILs) have a myriad of possible uses in industry and novel technologies but their wetting behaviour has not been studied in detail. This paper addresses the rate of spreading, thickness, and sensitivity to water (absorbed in the bulk IL and adsorbed at the solid surface) of a [Rmim][NTf₂] precursor film on mica. The IL droplets studied (emim, bmim, and hmim) showed very slow spreading on freshly cleaved mica that could not be attributed to the viscous spreading of the liquid. Instead, time-of-flight secondary ion mass spectrometry and atomic force microscopy imaging revealed good evidence of a precursor film that grows over similar time-scales.[1] The thickness of the precursor film could be accurately measured using nanoislands of octadecylphosphonic acid (OPA) on mica as an internal height reference. Increasing humidity enhances the rate of spreading, increasing the surface diffusion coefficient consistent with that observed previously for poly(dimethylsiloxane).[2] Adding water to the bulk IL phase prevents the slow spreading behaviour due to disruption of the interfacial ordering of the IL at the mica surface. Finally, it is shown that connectivity of nanoscale surface heterogeneity directly affects the macroscopic wetting behaviour and, when OPA islands become connected in a network (surface coverage ~ 60%) the slow spreading and precursor film formation is completely arrested.

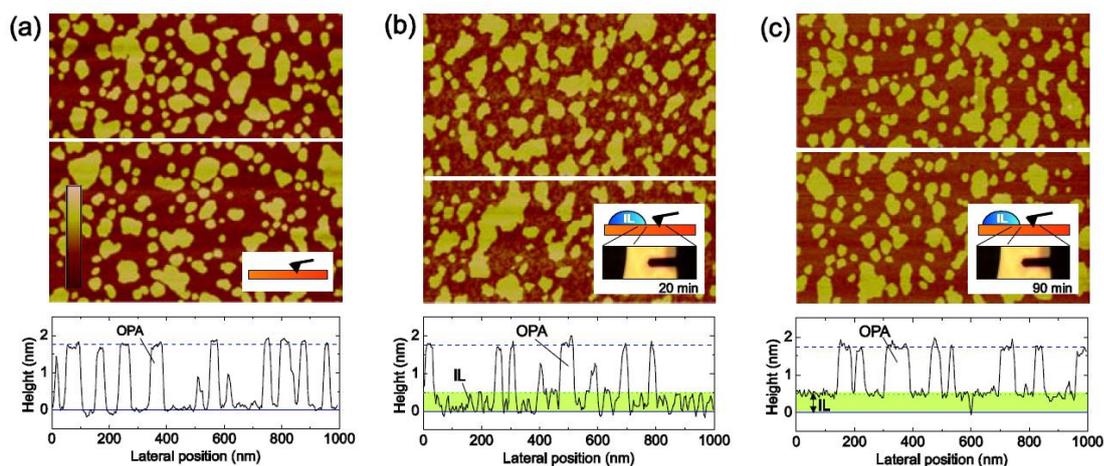


Figure: AFM images of (a) OPA islands on mica before placing an [emim][NTf₂] droplet, (b) ~ 20 min after droplet placement, and (c) 90 min after droplet placement. The green highlight in the line scans indicates the final precursor film thickness.

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OC110

Nano-structured Functionalised Porous Layers in Open Tubular 'Parallel Hole' Capillary Formats for Bioaffinity Applications

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Functionalised porous polymer phases for selective bioaffinity interactions have application within areas of both sensor and separation science. The surface functionalisation of so-called 'monolithic' porous polymer phases can take many forms, from simple surface chemistries, to grafted functionalised polymers, to nano-particle structured surfaces with attached chemical or biochemical functionality. In our laboratory we have utilised porous monoliths as scaffolds for presentation of functionalised nano-particles for selective surface interactions. The physical format of these scaffolds can vary considerably depending upon the application, from formation within capillary, as thin layers, immobilised within pipette tips, or to use within micro-fluidic platforms [1]. In our recent work we have studied the formation of open tubular structured thin layer porous polymers as a supporting scaffold for selective surface functionality, including bioligand functionalised gold nano-particles for flow through isolation of target biomolecules [2-4]. This presentation will discuss the latest developments in this area, specifically the surface functionalisation of a completely new format, namely 'parallel hole' micro-capillaries (single capillary with 125 individual parallel and isolated micro-channels of 5 µm I.D.). The internal walls of these micro-channels can be simultaneously modified with longitudinally homogenous bonded sub-micron porous polymer (e.g. PS-DVB) layers, and applied as scaffolds for variety of selective chemical and biochemical functionalities. The format provides a highly efficient structure for low pressure flow through applications such as bioaffinity isolation of biomolecules, whilst providing sufficient surface area and capacity for practical robust application. The presentation will include discussion on production and physical characterisation of these structures, together with demonstration of potential applications in separation science and selective micro-extraction.

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Designing and Evaluating Polymeric Electrode Materials for Bionic Devices

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Conventional platinum (Pt) electrodes experience poor cell integration *in vivo* leading to fibrous encapsulation which limits the efficacy and safety of implantable electrodes¹. Recent research has focused on the development of polymeric electrodes including conductive polymers (CPs) and conductive hydrogels (CHs) to improve cell interactions at the device interface. While CPs can improve the electrical properties of bioelectrodes², the expected improvement to cell integration has not been well supported *in vivo*¹. CHs have been shown to reduce interfacial stiffness², but little is known about their biological performance. Critical to understanding cell and tissue response is the need to evaluate the interactions of relevant, functional cell types as well as the potential for inflammation. *In vivo*, the first cell types which migrate to the electrode surface are glia such as astrocytes, however most studies evaluating bioelectrodes use only neural cell types including clonal PC12s², primary dorsal root ganglia³, and spinal neurons⁴. Each cell type has different physicochemical cues which support optimal interactions. As a result there is substantial variability in the literature describing *in vitro* cell interactions and *in vivo* performance of electrodes. This study assessed electrode material interactions using both PC12s and primary spinal neurons, as homogenous cultures and co-cultures with supporting glia.

CPs and CHs were fabricated using methods previously reported². The electrodeposited CP poly(3,4-ethylenedioxythiophene) (PEDOT) doped with pTS and the CH, PEDOT grown through a biosynthetic hydrogel (16 wt% polyvinyl alcohol crosslinked with 2 wt% heparin and 2 wt % gelatin) were prepared as detailed in Green et al² and compared with Pt. PC12 and Schwann cell studies were conducted over 5 days under neuronal differentiation conditions. Primary myelinating spinal cord neurons were prepared from fetal murine spinal cord and grown for 3 weeks⁴. Primary astrocytes were derived from murine neonatal forebrain. Immunofluorescent microscopy was used to analyse cell numbers and growth of neuronal processes.

The clonal PC12s were compatible with both CPs and CHs, but the CHs supported more cell attachment than CPs (28×10^3 compared to 17×10^3 cells/cm²). Both materials had significantly higher cell numbers than the Pt (9×10^3 cells/cm²). The CH contains gelatin which can improve cell attachment through active peptide binding. The rough topography of the CP is thought to encourage cell attachment. When cultured with Schwann cells all materials had increased PC12 attachment and neurite outgrowth compared to homogenous cultures, but no discernible difference was seen between CPs and CHs. Homogenous spinal neurons had poor or no attachment on any substrate. Neuron attachment and survival was improved when astrocytes were grown on the polymers prior to plating the spinal cord cells. The best axonal growth from co-cultured neurons was found on the CHs, but growth was generally considered poor on all electrode materials.

It is clear that different *in vitro* cell systems produce diverse biological responses to these materials. Co-cultures of either clonal or primary cells with appropriate glia showed improved cell attachment and differentiation, but less variation between materials. This more closely resembles *in vivo* performance. The CH was shown to be a promising option for improving bioelectrode properties.

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OC112

Tip-induced nanoparticle deformation during AFM imaging: implications for accurate sizing

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Measurements of nanoparticle height by atomic force microscopy (AFM) are a critical link in the measurement chain. At metrology institutes around the world, metrological AFMs – specialized instruments that use laser interferometry to monitor displacements – allow measurements of particle size to be linked directly to the SI metre, an important link that means equivalent measurements made around the world are accurate and comparable. The measurement model for deriving mean particle diameter from the particle heights in AFM images currently assumes, along with particle sphericity, that particles are incompressible, undergoing no deformation during sample preparation or imaging. This assumption has recently been questioned in the case of polystyrene nanoparticle reference materials.

Here, we report on a series of experiments in which the mean diameters of three commonly used nanoparticle reference materials, namely polystyrene, gold and silica, are derived from imaging in intermittent-contact (“tapping”) mode AFM to investigate how particle deformation may vary with imaging and particle parameters. Deformation was observed in diameter measurements of all three nanoparticle reference materials. Not unexpectedly, the degree of deformation varied with the particle material, with the greatest deformation observed for the polystyrene particles, less for the gold particles, and the least for the silica. The degree of apparent deformation varied with the maximum force exerted by the AFM tip during imaging. The tip force is controlled by the instrument’s cantilever free-air amplitude and feedback set-point imaging parameters. Significantly, the degree of particle deformation varied with particle size, with more dramatic deformation observed in particles less than ~30 nm in size. Also significant was the increasing deformation observed in gold and polystyrene particles as they were subjected to repeated scanning, suggesting that the observed deformation is predominantly plastic.

These results suggest that minimal force should be used in AFM imaging of nanoparticles. Furthermore, sample areas of interest should be imaged as few times as possible to minimize potential deformation effects due to the scanning process. AFM imaging parameters should be carefully specified and recorded, especially when comparing measurements.

OC113

Comparison of Eulerian and Lagrangian Colloidal Deposition in Laminar Flow

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Colloidal fouling involves particles depositing on a surface, often leading to adverse effects including: reduced heat transfer efficiency in heat exchangers and flow blockage in oil refineries. There exist two main approaches to model the deposition process: Eulerian and Lagrangian, but very few studies have investigated the quantitative difference between the two. This work aims to highlight key differences between the two modelling approaches in the context of the careful experimental work of [1,2].

Initial deposition rates of polystyrene latex particles in laminar flow have been studied with parallel plate [1] and stagnation point [2] flows; with a range of ionic strength of the buffer solutions. These studies compare their experimental results with numerical calculations (from the convection-diffusion equation in the Eulerian reference frame) and the Smoluchowski-Levich solution of the convection-diffusion equation.

We have simulated both parallel plate and stagnation point flow cases and tracked colloidal particles in the Lagrangian reference frame. DLVO theory was used to describe the interaction between the particles and the depositing surface: including the electrostatic double layer (repulsive) and van der Waals (attractive) forces [3]. Particles must overcome an energy barrier to reach the surface and deposit; this energy barrier depends on the ionic strength of the buffer. Brownian motion effects have also been investigated. [1] Sjollema, J.; Busscher, H. J. *J. of Colloid Interface Sci.* **1989**, *132*, 382-394.

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