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COLLOID AND
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SOCIETY

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2019 Abstracts

ACIS 2019 Complete Abstract Book

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Plenary Submissions

PL01

Ordering of hydrophilic and hydrophobized Silica nanoparticles in thin liquid films

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The presentation addresses ordering phenomena of Silica nanoparticles (NP) confined in thin films: 1) either pristine (hydrophilic) NP dispersed in thin aqueous films or 2) partially hydrophobized NP adsorbed at the air/water interface of foam films.

In the first part suspensions of pristine Silica NP are confined in a Colloidal Probe AFM (CP-AFM) between two solid surfaces. Oscillatory forces occur and the wavelength λ scales with the particle number density as $\lambda = \rho^{-1/3}$. An extrapolation towards high volume fractions shows that the $\rho^{-1/3}$ scaling law for λ ends up into a cubic lattice found for one-component systems like organic solvents, where $\lambda = d$ (d : diameter of molecules, particles etc.). A deviation from the exponentially decaying cosine function was found and can be described by an additional repulsion term [2,3] which will be discussed. Furthermore, it will be shown how oscillatory forces can be switched on and off by external stimuli [4].

Partially hydrophobized Silica NP order laterally at the interfaces of a free-standing film. Depending on the NP concentration they can form single aggregates or even percolation networks. The latter seem to stabilize foam films and even foams, *i.e.* so called Pickering foams [5,6].

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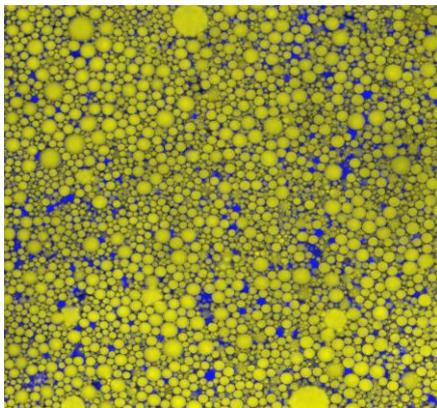
PL02

The science of taste

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Our interaction with the world, including food we eat, proceed via the five senses, one of which is taste proper. However, our general perception and appreciation of ‘taste’ arise as the brain’s multimodal integration of all sensory inputs folded with memories, expectations, emotions, etc. In my talk I will give an overview of the physiology, neurogastronomy, and gastrophysics of taste and exemplify the presentation with the science behind a specific basic taste, umami, and the tactile component of taste, mouthfeel. On the way we will see how colloidal and interface science come in all the way from the membrane receptor level to the texture of food.



(a microscopy image of mayonnaise)

Umami: Unlocking the Secrets of the Fifth Taste (O. G. Mouritsen and K. Styrbæk) Columbia University Press, New York, 2014.

Mouthfeel: How Texture Makes Taste (O. G. Mouritsen and K. Styrbæk) Columbia University Press, New York, 2017.

Keynote Submissions

KN01

The colloidal science of protein nanofibrils

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Protein Nanofibrils, also referred to as *Amyloid fibrils*, are protein aggregates, which can be generated from a broad class of proteins and peptides, including food-grade proteins, by unfolding, hydrolysis and one-dimensional self-propagation. At length scales above the well-established atomistic fingerprint of amyloid fibrils, these colloidal aggregates exhibit mesoscopic properties comparable to those of natural polyelectrolytes, yet with persistence lengths several orders of magnitude beyond the Debye length. This intrinsic rigidity, together with their chiral, polar and charged nature, provides these systems with some unique colloidal behavior, which share similarities and differences compared to other filamentous colloids. In this talk I will discuss our current understanding on the mesoscopic properties of amyloid fibrils at the single molecule level, the implication of their semiflexible nature on their liquid crystalline properties, and I will illustrate how this information prove useful in understanding their collective behavior in bulk and when adsorbed at liquid interfaces. By the careful exploitation of the physical properties of amyloid fibrils, the design of advanced materials with unprecedented physical properties become possible, and I will give a few examples on how these systems can ideally suit the design not only of complex food systems, but also of biosensors and biomaterials, catalytic and water purification membranes.

KN02

Connecting rheology to nanoscale structure of block copolymer micelle liquid crystals and nanocomposites

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At high polymer concentrations, solvent-selective block copolymer molecules self-assemble into concentrated micellar solutions that form highly-ordered, nanostructured, soft solids. Controlling the solvent quality allows for high densities of deformable (soft) particles to be achieved. Solvent stable nanoparticles dispersed in these soft solids will sample the solvent-swollen continuous structure providing a method to template, store, and define the environment of nanoparticulate material. Dispersed phase materials including metal oxide nanoparticles and globular proteins have been studied, providing composite systems in two interesting limits; hard particles dispersed in a dense dispersion of soft particles and a dense dispersion of soft particles with a bimodal level of softness. We characterize the impact of added nanoparticles on the local micelle packing, flow mechanism, and overall structure of the soft solid. These materials have rich phase behavior offering considerable potential in templating, transport properties and nanostructure control through both molecular design and processing.

KN03

Graphene oxide liquid crystal

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Graphene Oxide Liquid Crystal (GOLC) is a newly emerging graphene based material, which exhibits nematic type colloidal discotic liquid crystallinity with the orientational ordering of graphene oxide flakes in good solvents, including water. Since our first discovery of GOLC in aqueous dispersion [1], this interesting mesophase has been utilized over world-wide for many different application fields, such as liquid crystalline graphene fiber spinning, highly ordered graphene membrane/film production, prototype liquid crystal display and so on [2,3]. Interestingly, GOLC also allow us a valuable opportunity for the highly ordered molecular scale assembly of functional nanoscale structures. This presentation will introduce our current status of GOLC research particularly focusing on the nanoscale assembly of functional nanostructures. Besides, relevant research works associated to the nanoscale assembly and chemical modification of various nanoscale graphene based materials will be presented [4,5].

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KN04

Application of colloid and interface science in dairy systems

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Taste, texture, stability and performance during processing and in-use application as well as during consumption are key parameters, be it for creams, cream cheese, beverages or Mozzarella. All involve colloid and interface science but this cannot be considered in isolation. A consumer-led industrial research programme firstly considers and identifies the needs of the consumer via consumer research, and once the value proposition is identified and established, the key product features are considered. A multidisciplinary whole system approach explores the intercept between polymer and colloid chemistry and physics, interface chemistry, protein and lipid chemistry, enzymology, flavour chemistry and bimodal interactions. The complexity can be simplified when a Process – Structure – Properties model is applied. This presentation will place emphasis on colloid science and surface chemistry as part of a whole system approach to the development of dairy products.

KN05

Dynamic hybrid particles and materials

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Colloidal nanoparticles with inorganic cores and organic shells are dynamic at multiple scales other than their characteristic overall random walk. This talk will cover some dynamic aspects that are relevant for the preparation of functional materials from hybrid particles. First, I will discuss how surface diffusion on the surface of anisotropic metal colloids leads to shape changes, and how this diffusivity is affected by organic ligands. I will then turn to the dynamics in alkyl chain shell that stabilize certain hybrid particles in nonpolar solvents; we find that molecular phase transition of this shell can lead to reversible agglomeration of the entire colloid. Finally, I will consider the dynamic bending of ultrathin wires with an organic shell that lets them form ordered bundles. In the second part of my talk, I will discuss how to exploit mobile particles for functional materials: we combine bendable, ultrathin wires into fibers in a process that is similar to polymer spinning, and we print networks of wire bundles for transparent flexible electrodes. Finally, I will discuss how plasmonic particles with temperature-sensitive shells can be embedded in liquid inclusions to obtain solid “active composites” that change their color as a function of temperature due to reversible agglomeration.

Acknowledgments

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KN06

Soft carbon sheets: some new insights into an old material

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Graphene oxide (GO) sheets are made by exfoliation of graphite using century-old chemical reactions. Interest in this old material has resurged with the rapid development of graphene since 2004, as GO has been considered to be a promising precursor for bulk production of graphene. However, GO itself is a very interesting material in its own right. I will share a few curiosity-driven discoveries about GO, leading to new hypotheses and new applications of graphene-based materials. These include the discovery of GO's amphiphilicity, its use to construct 2D nanofluidic channels, the development of aggregation-resistant crumpled graphene balls, new forms of neat viscoelastic GO, and the application of GO and graphene as a materials-based solution to a difficult chemical problem in hair dyes.

KN07

Lipid self-assembly in bulk and at interfaces - Neutron and x-ray studies of non-lamellar phases and biomolecular interactions

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Well-defined non-lamellar lipid-aqueous system will help us understand the biological implications of curvature and confinement as well as develop new applications, for e.g. biomedical devices and targeted delivery. We will discuss how this can be achieved by deposition of lipids from solution followed by hydration. The properties of the formed layer will be discussed in terms of structure and dynamics as revealed by neutron and x-ray scattering techniques. We will show that we can form non-lamellar liquid crystalline surface films of different phases on the surface and that hybrid lipid polymer films can be formed with different properties compared to the neat lipid liquid crystalline layers. We will furthermore discuss how the lipid self-assembly structure can be change in desired way by adding a particular type of lipolytic enzymes. Here the (oil) triglyceride aqueous interface is important also for other processes like emulsification. Our results show that uptake of water in the triolein phase can occur and this can be affected by the presence of lipolytic enzymes [1]. The lipolysis-induced evolution of a particular structure formed by mixtures of lipids, which invoke different curvatures, is also controlled by the type of lipolytic enzyme. We demonstrated this by using highly structured cubic micellar (Fd3m) nanoparticles of 50/50 (wt%/wt%) soy phosphatidyl choline (SPC)/glycerol dioleate (GDO) [2].

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KN08

Developing globally accessible vaccines through scale-independent manufacture of liposomal adjuvants

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It is well recognised that vaccines remain the most cost-effective way to prevent infectious diseases and the development of effective adjuvants has enhanced vaccine efficacy and supported dose-sparing strategies. Amongst the range of adjuvant systems available, liposomes can effectively act as vaccine delivery systems and adjuvants. Pattern recognition receptors, including the Toll-like receptors (TLRs), are important in the induction and activation of two critical arms of the host defence to pathogens and microorganisms. However, incorporation or encapsulation of these TLR agonists within liposomes can promote local maintenance of the agonist at the site of antigen administration for optimal adjuvant activity to be achieved, without systemic distribution throughout the host. Resiquimod is a small (water-soluble) agonist of the endosome-located Toll-like receptor 7 (TLR7), therefore upon injection it will rapidly distribute throughout the body rather than staying at the injection site. Within our studies, resiquimod has been chemically synthesized with DSPE lipid to form a lipid-TLR agonist conjugate before further being incorporated within the cationic liposomes composed of dimethyldioctadecylammonium bromide (DDA) and the immune-stimulatory glycolipid trehalose 6,6'-dibehenate (TDB). The liposomes formulated with and without the conjugated TLR7 ligand displayed similar vesicle characteristics and conjugation of resiquimod resulted in strong retention of both resiquimod, as well as adsorbing the subunit vaccine. Following intramuscular injection a depot at the injection site was formed but this did not notably enhance immune responses compared to DDA:TDB liposomes without resiquimod. To ensure the translation of these liposomal adjuvants into cost-effective and globally accessible vaccines, we have also prepared these liposomal adjuvants using flexible and adaptive manufacturing processes, which can be scaled up and down in a rapidly responsive mode.

KN09

Polysaccharide materials based on polyelectrolyte interactions

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²*Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, Brisbane, Australia*

Polyelectrolyte complexes (PECs) form between cationic and anionic polymers through attractive electrostatic interactions. The nature of the PEC is affected by many factors including temperature, ionic strength and pH as well as polymer type, molecular weight and concentration. By manipulating these factors it is possible to form either weakly or strongly associated PECs that possess a range of physicochemical properties. Examples of PECs include coacervates and layer-by-layer assemblies. Both have found numerous applications in biomaterials science as, for example, drug delivery systems and coatings with properties tuned through control of the fabrication process.

The work presented will cover various aspects of developing polysaccharide-based materials, specifically using the biopolymers alginate, chitosan, and chemically modified alginate. Commonly used chemical characterisation techniques (FTIR and XPS) will be critically analysed for their ability to determine if strongly or weakly PECs form. Examples will be given of materials for drug delivery constructed utilising polyelectrolyte interactions as the main driving force. Findings relating to micron sized PECs for delivery of dermatan sulfate and sub-micron sized PECs for delivery of lactoferrin will illustrate how both the size and drug release rate can be tuned by the fabrication parameters.

KN10

The importance of classical soft matter physics in the development of new nanomaterials

Lauren Taylor¹, presenting on behalf of Matteo Pasquali¹

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Upon their introduction, certain classes of nanomaterials such as carbon nanotubes (CNTs) and graphene appeared completely disjointed from the area of soft matter—in part because forming stable fluid phases with such materials appeared nearly impossible. In this talk, I will discuss the importance of classical soft matter physics in the development of high-performance CNT materials. I will describe how classical concepts from colloids and polymer science, such as intrinsic viscosity, persistence length, liquid crystalline phase transitions, are key to understanding and controlling CNT fluid phases, and how this degree of control is now yielding a new class of soft materials that combines the most attractive traits of polymers (mechanical softness, easy flow processing) with the properties of conductors and semiconductors, that had remained so far elusive. I will discuss how these advances on controlling CNT phases have allowed rapid progress on the understanding and processing of graphene and graphene oxide. Finally, I will offer my perspective on the advantages and disadvantages of two-dimensional vs. one-dimensional building blocks for multifunctional nanomaterials.

Invited Submissions

IN01

Revealing the nanostructure of fat crystals by atomic force microscopy

Nan Gao¹, Damien Sebben¹, Graeme Gillies², Marta Krasowska¹, David Beattie¹

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Habit and morphology of triglyceride crystals are critical factors in the formulation of lipid-based colloidal systems such as pharmaceutical formulations and dairy products. Until now, triglyceride crystal characterisation has been largely performed using thermal analysis, scattering techniques, and electron microscopy. We present the use of Atomic Force Microscopy (AFM) for the 3-dimensional mapping of the nanoscale morphology of single glyceryl tristearate (tristearin) crystals ¹ and triglyceride crystals isolated from milk fat using fractionation techniques ². We show in great detail the topographical features of fat crystals not apparent using other techniques, and investigate the effect of solvent-mediated recrystallization on crystal morphology, and the influence of fractionation protocols. The use of AFM circumvents the disadvantages of electron microscopy, such as melting of triglyceride crystals and freezing of aqueous phase residue. The approach presented in this work gives new physical insight into the 3-dimensional features of the crystals, which will have an influence of their behaviour in lipid-based soft matter and colloidal systems.

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Interface properties and reactions of boron nitride nanosheets and nanotubesYing Chen¹, Luhua Li¹, Srikanth Mateti¹, Mokhles Rahman¹, qiran cai¹, Baozhi Yu¹¹Deakin University, Geelong, Australia

Boron nitride (BN) nanosheets are an important member of two-dimensional (2D) nanomaterials and have a same structure to graphene. BN nanosheets have many properties distinct to graphene and unique applications not available to graphene. This presentation presents our recent research in BN including special mechanical properties [1], superb surface adsorption capability [2], functionalization [3], and their applications as reusable substrates for surface enhanced Raman spectroscopy (SERS) [4], interlayers for improving cycling life of Li-S batteries [5]. Many applications require a colloidal solution of BN nanomaterials for producing membranes, thin films, and coatings. However, this is a big challenge because of the super-hydrophobic nature of BN nanosheets and nanotubes, it is difficult to disperse them in water directly. We overcame this challenge by attaching a number of NH or OH groups using a new in-situ reactive ball milling process that simultaneously exfoliates and functionalises nanosheets. The functionalised BN nanosheets can be dispersed into water, polymer and other solutions forming stable colloidal systems with very high BN contents [3]. From these solutions, BN membranes, thin films and composites have been produced. The BN nanosheet membranes are used to build a fluidic device with nano-channels for ion separation [6] and an electric generator [7]. BN nanosheet coating shows excellent corrosion resistance. Further information can be found at https://www.researchgate.net/profile/Ying_Chen191.

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IN03

Scalable graphene chemistries for processing and fabrication

David Officer¹

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Graphene, a nanocarbon with exceptional physical and electronic properties, has the potential to be utilised in a myriad of applications and devices. To realise this, the development of scalable chemistries that allow the production of graphene dispersions is required that facilitates processing and fabrication in such a way that the inherent properties of graphene are maintained within the material structures or devices. This will involve chemistries for the most part that enable efficient graphene integration with a host polymer, and that result in formulations with rheological properties that allow the use of fabrication tools such as fibre spinning or printing.¹

We have developed chemical exfoliation methods of both single and multi layer graphene oxide and graphene itself that afford processable dispersions in both aqueous and organic solvents. We have then explored their use for the preparation of a variety of material composites, materials useful for the fabrication of graphene-containing structures and devices.^{2,3,4}

In this lecture, we will discuss the preparation and application of these processable graphene dispersions, and the relative merits of each approach to the development of graphene composites and devices.

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IN05

Photocatalytic activity at interstitial sites across vertical-aligned graphene patterned surfaces

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Vertically-grown graphene (VGN) walls, generated by chemical vapour deposition, offer unique opportunities to study the impact of functional groups densities and sp² bonding on the properties of graphene. The high levels of edges generated and exposed in this configuration, compared to horizontally graphene nanosheets, allow for studying electronic transfers and recombination between individual graphitic sheets.

In this communication, the photocatalytic activity of vertically-aligned graphene nanosheets grown across both silicon wafers and carbon fibre substrates were evaluated for the degradation of organic contaminants. The impact of the growth conditions on the VGN was correlated to the VGN walls density and microstructure, while the electronic properties of the materials were investigated to explain the unusual photocatalytic performance of the materials upon UV irradiation. The stability of the photocatalytic performance was confirmed through cyclic testing of the catalytic evaluation. This strategy opens up new opportunities in advanced band gap engineering across carbon materials with potential in environmental science, reactive conductors and optoelectronics applications.

IN06

Graphene oxide modification of natural materials and biomaterials for various water treatments

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There is a strong societal push to use more sustainable materials, particularly those that are natural or made from biomaterials. The issue is that these materials, in themselves, are not very useful in practical applications due to lack of functionality or structural properties. When the hydrophilicity of these systems, and that of graphene oxide (GO) are matched, GO makes an exceptional additive for improving property/function of natural materials and biomaterials. This talk will discuss 3 materials, namely natural clinoptilolite-rich zeolite powders, sodium alginate and regenerated celluloses and their modification with graphene oxide for improved properties. Firstly, the modification of zeolite powders with GO nanosheets then grafting a diazonium salt (4-carboxybenzenediazoniumtetrafluoroborate) to the GO surface will be discussed. This hybrid material was then characterised using Raman spectroscopy, Fourier transform infrared (FTIR) spectroscopy, and thermogravimetric analysis (TGA). Adsorption performance of a dye, rhodamine B, from aqueous solutions was then evaluated. The adsorption behavior was fitted to a Langmuir isotherm and shown to follow a pseudo-second-order reaction model. Secondly, the adsorption performance of calcium alginate (Ca-Alg₂) and Ca-Alg₂ with encapsulated graphene oxide (Ca-Alg₂/GO) gel bead adsorbents will be discussed for the successful removal of Cu²⁺ ions from aqueous solution. Different adsorbent doses, Cu²⁺ concentrations and contact times were investigated using equilibrium and kinetic studies. The adsorbents were characterised using FTIR spectroscopy, TGA and focussed ion beam scanning electron microscopy (FIB/SEM). The equilibrium adsorption data were fitted to Langmuir isotherms and the maximum adsorption capacities of the Ca-Alg₂ and Ca-Alg₂/GO gel beads were found to be 42.7 mg g⁻¹ and 60.2 mg g⁻¹, respectively. Finally, the talk discusses the fabrication of spun fibres and membranes of regenerated celluloses blended with GO at different loadings. The fibres and membranes were evaluated for tensile strength, swelling, flux and absorption studies.

IN07

EGO/PDMS nanobeads composites for highly stretchable and sensitive wearable tactile sensor

Yulin Zhong¹

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The advancement in the 3D printing of multifunctional devices would accelerate the development of various wearable electronics, including smart sensors and human-machine interfaces. Polydimethylsiloxane (PDMS) elastomer is widely used in a wide range of wearable electronics. However, it has proved challenging to 3D print PDMS based electronics with complex structures and multifunctionality, due to its low elastic modulus and the need for support during the printing process. Herein, a facile, cost-effective and efficient method is presented for the direct ink writing of conductive electrochemically-derived graphene oxide(EGO)/PDMS nanobeads composites in which the PDMS nanobeads were fabricated through a simple emulsification process. Due to the unique hybrid structure of nanocomposite, the 3D printed tactile sensor demonstrated ideal linearity, high reproducibility and excellent sensitivity which can serve as a health-monitoring device to detect various human motions, ranging from finger bending to radial pulse. The strain sensor is then interconnected via printed conductive traces to yield soft electronic devices that may find potential application in wearable sensor, soft robotics, and biomedical devices.

IN08

Molecularly engineered graphene surfaces for bio-applications

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Controlling surface interactions between an immobilisation surface and enzymes can be used to control enzyme activity, including substrate selectivity. Here we use modified graphene as a controllable surface to improve the activity and selectivity of enzymes. In addition to fundamental understanding of the ability of surfaces to modify enzyme activity, the graphene-lipase system offers a new controllable immobilised enzyme catalyst for industrial applications. The research will lead to improved understanding of the basic mechanisms of protein self-assembly and interaction with surfaces to control enzyme functionality, which will be utilised to produce next generation immobilised catalysts, bioelectronics and biosensors.

IN09

Application of graphene oxide membranes

Rakesh Joshi¹

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We have studied separation, purification, water absorption and sponge like behavior of graphene oxide (GO). Using GO membranes, we have achieved an extremely high-water flux in practical conditions with ~100% rejection (or below detection limit) of targeted toxic molecules. We have studied the water adsorption behavior of graphene oxide and our highly reproducible results suggest that GO membranes completely outperform silica gel, a commercial benchmark desiccator. On using GO as intercalation template, we noticed a highly recurring sponge like behavior to foreign molecular/ionic species. The interlayer spacing of graphene oxide increases to a higher value on intercalating, depending on the size of species, followed by obtaining an original value on desorption. The observed highly reproducible behavior enables multiple possible applications of graphene oxide.

(B. Lian, Y. You, X. Jin of UNSW Sydney and H. Bustamante of Sydney Water have significantly contributed to this work. Majority of the results have been published or submitted for publication in various Journals)

IN10

Electrified layered organic-inorganic hybrids for capacitive storage

Dawei Wang¹

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We report the recent discovery of the fast ion intercalation in a new type two-dimensional organic-inorganic hybrid structure, as well as the fine molecular tailoring of the interlayer chemistry.

A room-temperature self-assembly procedure was developed to produce a new 2D hybrid structure with expanded periodic stacking distance which is also highly solvated. The solvated large gallery allows the swift ion storage. This hybrid 2D structure consists of conductive polymer nanoribbons that are cross-linked by inorganic tungstate molecules. A simple solvent-exchange process enables the use of this material for either aqueous or non-aqueous energy storage, which shows the self-adaptive property and automated response to electrolyte wetting in electrochemical devices.

Combining a series of electrochemical and spectroscopic methods, we successfully identified the double layer dominant interface charging mechanism in this material, and also determined the stable electrochemical window. Based on these findings, we have been able to design ultrathick electrode to achieve large volumetric performance in an asymmetric supercapacitor.

IN11

Surface chemistry for 2D materials and applications

Zongyou Yin¹

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Nano science and technology offer a vast and fascinating playground to explore the novel properties of nanomaterials for the advanced applications. First, in this talk, I will present diamond-based surface charge doping based on using hydrogenated MoO₃ layer as a novel efficient sustainable surface charge acceptor for diamond transistors. Second, I will present the modified 1T'-WS₂ exhibits far better and more stable electrocatalytic hydrogen evolution than 2H-WS₂ in acid electrolyte. After perform extreme durability testing continuously over one month, 1T'-WS₂ exhibits super durability with an half-life of ~ 46 days. This talk highlights the design and development of surface chemistry to tune the interface activities for advanced electronics and energy conversion.

Colloidal capsules from graphene oxide Pickering emulsionsRico Tabor¹¹*School of chemistry, Monash university, Melbourne, Australia*

For some time, it has been known that graphene oxide and related 2-dimensional nanomaterials can stabilise emulsions and foams by adsorbing at the oil–water interface [1]. Emulsions stabilised by graphene oxide show remarkable long-term stability, and can be tuned by changes in solution conditions such as pH, offering pathways for reversible flocculation and redispersion, and making them interesting candidates for a range of applications. However, the mechanism and thermodynamics of adsorption of these 2D materials at interfaces is poorly understood, and limits the design of systems for specific purposes. Using a combination of tensiometry, atomic force microscopy and X-ray reflectivity, we have shown that the adsorption of graphene oxide at air–water and oil–water interfaces is not spontaneous, but can be enhanced by the addition of small amounts of surface active small molecules [2]

In most cases, emulsification of oil in water with graphene oxide gives simple oil-in-water emulsions [1]. However, for certain oils, carefully engineered solution conditions result in single-step production of multiple emulsions [3], leading readily to multi-compartment capsules through polymerisation of the outer droplet interface. Controlling the outer ‘skin’ of these capsules allows for controlled release of active agents contained within, and we provide proof of concept studies showing that release of aqueous actives can be modulated by the shell thickness, offering routes to controlled release of agrochemicals, etc.

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IN14

Chemical and topological design of high-performance chemically modified graphene films

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Paper-like graphene films are expected to have applications in flexible electronics and lightweight structural materials. The realization of these applications is partly relied on the mechanical properties and/or electrical conductivity of graphene films. This presentation will introduce the rational design of ultrastrong and highly conductive graphene films, and the potential applications of the resultant graphene films in flexible electrodes. Particularly, I will describe the effects of chemical and topological structures of the building block (reduced graphene oxide) and the film microstructures and compositions on the mechanical and electrical properties of the graphene films. The results would give a guideline for the preparation of high-performance graphene films.

IN15

Ultralight graphene-based elastomers

Ling Qiu¹

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Graphene possesses a combination of exceptional mechanical and electrical properties. These extraordinary properties make graphene an excellent building block for assembling macroscopic materials for widespread applications. This talk will first introduce the synthesis of extremely low density graphene-based elastomers by design and engineering of their hierarchical cellular structure. This talk will then focus on discussing their dynamic mechanical and electromechanical properties. This new class of elastomer reveals a combination of extremely low density, superelasticity and good electrical conductivity, which shows great potential for making next generation flexible electronics.

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IN16

Nanoice sinks and melts under the influence of charge and van der Waals forces

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It is well known that icebergs float at the water surface. But the weaker buoyancy of nanoice is opposed by repulsive van der Waals forces which cause nanoice to sink several nm below the water surface. This phenomenon is enhanced by an unexpected formation of charge at the ice surface. Formation of an layer of adsorbed ions at the ice surface provides sufficient repulsion to cause nanoice to sink to an equilibrium distance as far as a micron below the water surface, depending on pH and ion concentrations [1]. The formation of this exclusion zone free of nanoice occurs when ice particles are smaller than 10 μm in size.

Ice confined together with air in nanopores undergoes partial melting with the formation of a liquid water layer due to the influence of 4-phase van der Waals interactions. Metallic inclusions in the pore walls may induce complete melting of ice when the air layer is 1.5-5.5 nm thick [2]. Conversely a layer of ice up to 8 nm thick may stabilise at the water-silica interface [3].

We expect these phenomena have implications for the growth of microbes in the exclusion zone at the water surface, free of nanoice, and for the weathering of rock and formation of mineral deposits due to water and ice in nanopores.

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IN17

Soft plasmene nanosheets: from design to applications

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My nanobionics research lab concentrate on the design of soft/hard nanohybrids based on metallic nanoparticles capped by soft ligands including DNA, polymer and alkyl molecules. We have successfully applied such soft particles to four major directions: (1) assembling soft plasmonic nanoparticle superlattice sheets (soft plasmene sheets); (2) fabricating electronic skins (e-skins) for wearable sensors; (3) fabricating soft energy devices; (4) DNA aptamer-targeted and light-controlled drug delivery.

In this talk, I will focus on the discussion of the first project for producing soft, elastic, two-dimensional plasmonic nanoparticle superlattice sheets (soft plasmene sheets) by self-assembly of polystyrene-capped metal nanoparticles. The soft nanosheets could be folded into 1D nanoribbons and 3D origami, and they can serve as a new-class SERS substrate which is soft, elastic and surface-attachable. This enabled the direct chemical identification on topologically complex surfaces such as banknotes and coins, and application as new-generation of anti-counterfeit security labels and ultrathin flat lens.

2D Materials of unique nano- and micro-structures for energy harvesting

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¹Deakin University, Geelong, Australia ²Wuhan Textile University, Wuhan, China

Due to the rapid development of science and technology, smart phones gradually become indispensable to our fast-paced life, consuming a significant amount of electricity. The chargers of smart phones are commonly required to plug in to a power point, which has highly restricted the portability of the purpose of phones and presents life-threatening dangers if no charging facilities or electricity were available in remote areas. Textile-based triboelectric nanogenerators (Tex-TNEGs) can convert the common mechanical energy from human motion into electrical energy, which has the potential to provide smart phones with energy from day-to-day activity. Herein, graphene was incorporated into polyurethane (PU) fibres via wet spinning method to form composite fibres that can be fabricated into any type of fabric to form a Tex-TENG. The PU/graphene composite fibres could act as both friction and electrode materials, which renders the TENG flexibility, durability and waterproofness. Furthermore, this Tex-TENG can also serve as a self-powered motion monitoring system, recording the amplitude and frequency of human motion at real time.

IN20

Graphene suspension for polymer composites

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Of all engineering materials, polymers have witnessed rapid increase in applications over the past decades due to their low manufacturing cost and decent specific strength. However, polymers are limited by low absolute stiffness and strength and lack of functionality such as electrical and thermal conductivity. Processing polymers with nanomaterials holds great potential to address these limitations.

In spite of extensive studies of utilizing carbon nanotubes and silicate layers to address the limitations, the rise of graphene now provides a more promising candidate due to its exceptionally high mechanical performance, electrical and thermal conductivities, and specific surface area. My research team since 2008 has conducted extensive research of developing new graphene platelets and using them for processing of epoxy, elastomers and conducting polymers. Graphene platelets contain only 7 atom% oxygen and have a thickness of 2–4 nm depending on the suspension medium for measurement. They have a Raman I_d/I_g ratio of 0.07, corresponding to an electrical conductivity of 1456 S/cm measured by a four-probe method. These platelets can be treated further by oxidation for the development of graphene/polymer composite hydrogels. A percolation threshold of electrical conductivity was found at 0.4 vol% graphene for these hydrogels. At 1.0 vol%, Young's modulus and compressive strength were respectively enhanced from 1.64 to 19.03 MPa and from 0.37 to 6.90 MPa, corresponding to 1060% and 1765% improvements. These improvements were explained from the perspectives of the graphene sheets' dispersion and their interaction with the polymer and water molecules. It is worth noting that the addition of graphene improved the hydrogel pH sensitivity.

IN21

Design strategies for nanomaterials to cross lipid bilayers

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Design of nanomaterials able to cross lipid bilayers is a challenging task in nanotechnology. Large variety of shapes, sizes and surface coatings are used for the design of nanomaterials to overcome this barrier. However, the potential barrier is quite high for carbon nanotubes and nanoparticles to cross the lipid bilayer to translocate by thermal motion. It is generally accepted that small hydrophobic nanoparticles are blocked by lipid bilayers and accumulate in the bilayer core, while nanoparticles with sizes larger than 5 nm can only penetrate cells through a slow energy-dependent processes such as endocytosis, lasting minutes.

In one example, we show how variation of hydrophobicity of the nanoparticles can lead to passive translocation of nanoparticles through lipid bilayer. This adsorption transition through reversible destabilization of the structure of the bilayer induces enhanced permeability for water and small solutes.

In another example, we demonstrate that lipid-covered hydrophobic nanoparticles may translocate through lipid membranes by direct penetration within milliseconds. We identified the threshold size for translocation: nanoparticles with diameters smaller than 5 nm stay trapped in the bilayer, while nanoparticles larger than 5 nm insert into bilayer, open transient pore in the bilayer. Using the Single Chain Mean Field (SCMF) theory a mechanism of passive translocation through lipid bilayers is proposed. Observing individual translocation events of gold nanoparticles with 1-dodecanethiol chains through DMPC bilayers we confirm the particle translocation and characterize the kinetic pathway in agreement with our numerical predictions. Mechanism relies on spontaneous pore formation in the lipid bilayer. The observed universal interaction behaviour of neutral and chemically inert nanoparticles with bilayer can be classified according to size and surface properties.

Oral Submissions

OC001

Food Materials Science @ ANSTO

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On a daily basis, the most ubiquitous form of soft matter with which we interact is food. When designing new food products for the market-place, it is important to understand the relationships between the form and functional properties of food constituents, including food structure, nutrition, physiological and sensory properties. The creation of novel functionalities of active ingredients in complex food systems requires knowledge of not only the structure of native agricultural materials but also the changes in their structure across a wide range of length scales brought about by food processing. It is the inherent complexity of modern food systems that calls for interdisciplinary scientific approaches to be applied. To tackle many of these issues, ANSTO commenced the 'Food Science' Programme in 2005. The programme was conceived as having a focus on neutron scattering but naturally and necessarily utilises ANSTO's broader infrastructure in X-ray scattering and diffraction, electron microscopy, the National Deuteration Facility and the Australian Synchrotron. This presentation will describe several examples including starch, oleogelators, triglycerides, digestion and food processing.

For a full list of publications, see www.ansto.gov.au/research/programs/other/food-science/highlights

OC002

Droplet-stabilised emulsions: colloidal and oxidative stability advantages

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Droplet-stabilised emulsions (DSEs) are a novel colloidal structure in which lipid nanodroplets or nanoparticles stabilise the interface of a microscopic lipid droplet (Ye et al. 2013 Langmuir 29, 14403). This nested structure confers unique advantages due to high interfacial adsorption energy, similar to Pickering emulsions, and a semisolid networked interfacial structure.

We have now defined the formulation and processing parameter space for producing food-grade DSEs, which opens up new applications in designing healthy, clean-label food products.

DSEs were produced with protein-emulsified surface droplets/particles consisting of olive oil, palm oil or trimyristin, thus giving liquid, semicrystalline and crystalline molecular structures at ambient temperature. The core droplet was high-linoleic acid safflower oil, which is a good source of polyunsaturated fatty acids (PUFA). Surface droplets/particles were produced by homogenising at 400/50 bar (Homolab2, FBF Italia) and DSEs were formed with a high-shear mixer (D-130, Labserv) operating at 6000 rpm for 5 min. DSE structure was characterised with confocal scanning laser microscopy (Leica DM6000B ST5), static light scattering (Malvern Mastersizer) and confocal Raman microscopy (WITec) with microfluidic droplet isolation. PUFA oxidation in the presence of light and aqueous Fe²⁺ (oxidation accelerants) was measured for 9 days via conjugated dienes (CD), lipid hydroperoxides and hexanal, which are primary, secondary, and tertiary oxidation products.

DSEs had good structural integrity, although some aggregation and flocculation were observed with liquid and semicrystalline surface droplets. Oxidation was slower in all DSEs, as compared with composition-matched conventional emulsions. Crystalline trimyristin surface particles provided the highest oxidation resistance, with up to 55% reduction in CD area-under-the-curve, as well as high structural integrity. With confocal Raman microscopy we were able to verify the location of antioxidants incorporated in either the shell or core lipids.

Droplet-stabilised emulsions are a promising new colloid with applications in food, pharmaceutical and personal care.

OC003

Seaweed polysaccharides as excipients and functional food ingredients

Damien Stringer¹, [Helen Fitton](#)¹, Samuel Karpiniec¹, Ahyoung Park¹

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Marine macroalgal polysaccharides have long been associated with food and beverage formulations, most often through the use of the gelling carbohydrates - carrageenan and agar from red seaweeds - in thickening and emulsifying roles. Here, we will discuss the growing use of fucoidans - non-gelling sulfated polysaccharides from brown seaweeds - in functional food and medical device applications. Fucoidans have grown in use in the past decade as validated commercial sources of fucoidans have become available and achieved regulatory approvals. Recent studies to be discussed here include the potential use of fucoidan extracts in coating, secondary drug release and pathogen binding applications.

Influence of a pH-responsive electroactive amphiphile on the formation of lipid cubic phases

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Lyotropic liquid crystals (LLCs) based on self-assembling lipids have been the subject of extensive research as they can form highly-defined structures with tuneable properties.¹ Transitions between mesophases or from ordered to disordered phases can be controlled by incorporating a stimuli-responsive additive.^{1,2} A pH-responsive, tetra(aniline)-derived (TANI) amphiphile, (TANI-PTAB), that self-assembles in water into nanowires in the emeraldine base (EB) state has been prepared (Figure 1).³ Upon doping with acids (with different molecular volumes), TANI-PTAB in the emeraldine salt (ES) state forms different structures that can be related to the packing parameter of the doped compound.⁴ It may therefore be possible to use this change in packing parameter of TANI-PTAB with doping to control the self-assembled structures of a lipid-system. In this study, TANI-PTAB was synthesised and incorporated into the cubic phases of monoolein. Small-angle X-ray scattering of the LLC demonstrates that the addition of increasing concentrations of TANI-PTAB in the EB state swells the phase from $Pn3m$ to $Im3m$ (Figure 1), while addition of a dopant inhibits this transition and the LLC stays in the $Pn3m$ phase.

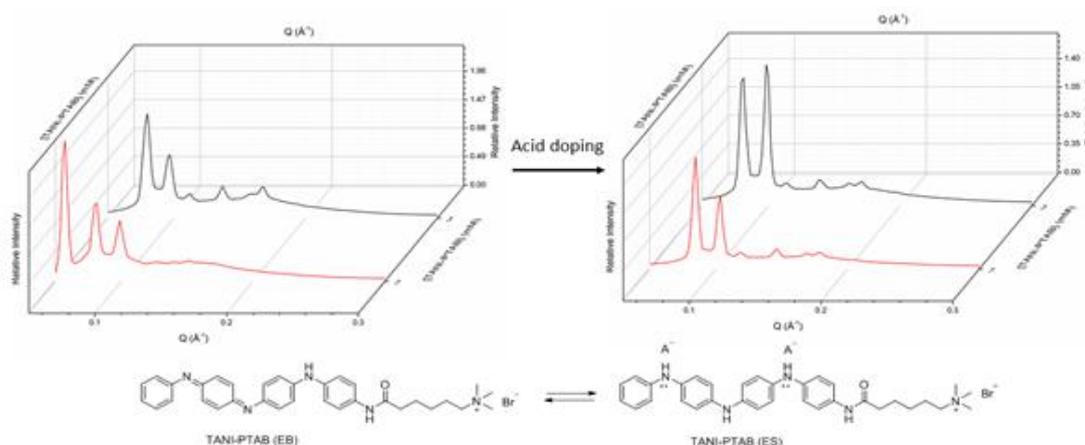


Figure 1. (Above) SAXS spectra of monoolein, pentaerythritol propoxylate (PPO) and TANI-PTAB (3 and 7 mM) in the EB and ES state. (Below) Structures of TANI-PTAB (EB) and TANI-PTAB (ES).

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OC005

Agglomeration of ultrafine hydrophobic particles using a high internal phase emulsion binder with thin permeable oil films

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¹*the University of Newcastle, Newcastle, Australia*

The recovery and concentration of high value ultrafine base and precious metals is difficult to achieve, even via froth flotation. Inspired by oil agglomeration, a novel process involving the use of a high internal phase water in oil emulsion binder has been developed to address this challenge. The research has focussed on the agglomeration via batch mixing, and by a novel continuous process, so far covering selective agglomeration of coal, magnetite, and silica.

The use of the binder significantly reduces oil consumption by over an order of magnitude compared to conventional oil agglomeration. The agglomeration is ultrafast, with the ability to recover hydrophobic particles below 1 μm in size in a few seconds. We believe that the emulsion structure is responsible for the efficient and highly effective particle recovery. The highly concentrated dispersed aqueous phase, which exists as tightly packed droplets, gives rise to a network of thin, permeable oil films. The oil films work to cover the particles during the agglomeration process, providing a large surface area for particle deposition and adhesion.

In order to build new knowledge and understanding of the performance of the binder it is necessary to understand the factors governing the thickness of the oil film. Reducing the film thickness, by refining the binder to achieve smaller drop sizes, increasing the volume fraction of the internal phase, and promoting water permeation, has resulted in a reduction in the required binder addition to achieve agglomeration.

Under extreme conditions, the potential for the oil films to thin appears to be underpinned by a structural limitation of ~ 10 nm. Experiments have therefore been conducted to examine the effects of surfactant concentration within the organic phase of the binder, adsorption and micelle formation within the oil films, to explain the limits on film thinning.

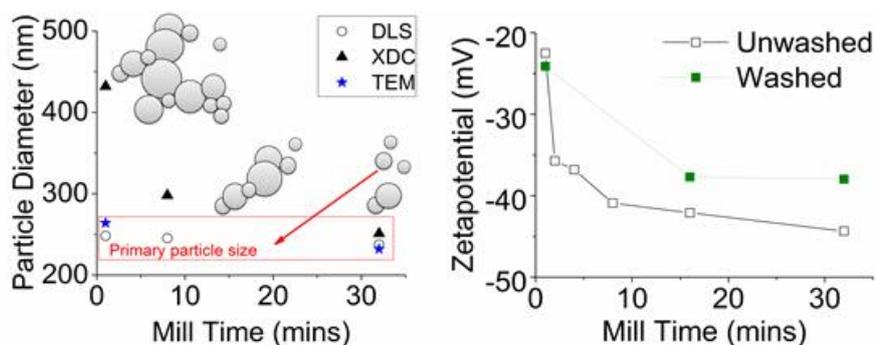
OC006

Characterisation of dispersion interactions between aluminium-doped titania pigment particles and polyphosphate salt during milling

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Polyphosphate salts are widely used during mineral processing, for example they are added to the titania pigment suspensions during milling, to improve the dispersion properties and reduce suspension viscosity. However, aqueous polyphosphate solutions are not stable under high temperature, acidic or basic pH, and even in the presence of some metal ions. Thus questions remain regarding the stability of the polyphosphate-pigment interactions and the influence of milling time on the structure and density of polyphosphate dispersants on the surface of titania. Hence, investigated is the characterisation of industrially produced alumina-doped pigment particles, milled for different periods of time in the presence of sodium hexametaphosphate (SHMP). Transmission electron microscopy (TEM) indicated that prolonged milling times led to the production of titania particle fines in the order of 10 nm electrostatically attracted to larger particles, where no change in the crystal structure was observed. The average hydrodynamic diameter calculated from dynamic light scattering (DLS) showed no change in primary particle size (~250 nm) with respect to milling time when fitted using a second exponential and correlated closely with the primary particle size obtained by TEM. The TiO₂ was found to have an isoelectric point (iep) in the range of pH 3 to 4.5, with an increase in milling time leading to a lower pH_{iep}, indicative of an increase in SHMP coverage, which was further supported by an increase in phosphorus content by X-Ray fluorescence (XRF). Phosphorus content and zeta potential analysis before and after centrifugal washing, showed that SHMP was partially removed or hydrolysed for the longer milled pigment samples, whereas no change was observed for shorter milled samples. It is thought that extended milling times lead to the hydrolysis or other structural changes within the dispersant from the high energy milling conditions, allowing easier removal of SHMP for longer milled pigment.



OC007

Energy-landscapes of chemically anisotropic particles at an air-water interface

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Recent advances in fabrication techniques have allowed for synthesis of anisotropic Janus particles with precise control of the amphiphilicity of the particle and the surface wetting properties on each hemisphere. Interfacial assembly of anisotropic particles is of particular interest as these confined particles can be used to template microstructures in a bottom up fashion. The fluid-fluid boundaries can trap colloids, orienting particles in the direction normal to the surface and patterning particles in the plane of the interface. The ability to pattern particles at interfaces has a multitude of applications such as achieving optical properties, making antireflective surfaces, improving the resolution of E-paper displays and creating water repellent materials. Furthermore, anisotropic particles at interfaces can be applied as emulsion stabilizers and catalysts. In all of these applications, the amphiphilicity of Janus particles plays an important role in influencing particle orientation, stability and assembly at the interface. Additionally, understanding the free-energy landscape of Janus particles at an interface can help explain and predict particle behavior under different circumstances. We explore the behavior of gold-capped silica Janus particles at the air-water interface, quantifying how the degree of amphiphilicity and orientation of gold-capped silica Janus particles affects behavior at the air-water interface for an individual particle as well as a particle-laden interface. Colloidal AFM experiments have been conducted by fixing Janus particles to a cantilever at various orientations. Subsequently, force is measured as the particle interacts with and is wet by the air-water interface of a surface immobilized bubble. These experiments allow for quantification of surface forces, adhesion, contact angle, and give insight as to how the energy landscape of the particle changes with orientation and amphiphilicity.

OC008

Understanding the interfacial behaviour of bile salts, a key to their role in lipid digestion

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Regulating fat (dietary lipid) digestion to tackle the ongoing obesity crisis has become a pressing issue. Bile salts (BS) are biosurfactants produced in the liver and released into the small intestine, which play key roles in lipid digestion and absorption: they facilitate enzyme adsorption to fat droplet interfaces and remove insoluble lipolysis products from the interface, carrying them to the gut mucosa for absorption. It is suggested that BS structural diversity is responsible for these contrasting functionalities¹. Our objective is to correlate BS molecular structure with their interfacial properties to shed light on the mechanisms governing their different functions in lipolysis. Two BS constituting 15% of human bile were selected, sodium taurocholate (NaTC) and sodium taurodeoxycholate (NaTDC), which differ only by one hydroxyl group but display contrasting adsorption/desorption dynamics¹. Their adsorption behaviour at the air/water interface and their interaction with a phospholipid monolayer – a preliminary mimic of physiological fat interfaces – were assessed using a Langmuir trough and ellipsometer, and the interfacial film structure characterised by Brewster angle microscopy, X-ray and neutron reflectometry. NaTC was found to exhibit a high affinity for the interface, while NaTDC was shown to remove DPPC molecules from the interface, through a dynamic exchange. NaTC may thus facilitate enzyme adsorption onto fat droplet surfaces, whereas NaTDC may displace lipolysis products from the interface. BS micellisation was studied using pyrene fluorescence spectroscopy and small-angle X-ray scattering. NaTC was found to form smaller micelles from a higher critical micelle concentration (CMC), compared to NaTDC. Interestingly, BS interfacial properties correlate with their bulk aggregation: both BS preferentially adsorb at the interface below their CMC and desorb above that value.

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OC009

Controlling liquid crystalline structure formation in digesting milk-like emulsions

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Milk is nature's emulsion for delivering fats and fat-soluble nutrients to infants and remains a mainstay of the adult diet thereafter for many. The milk fats that deliver these nutrients comprise 98% triglycerides each with three of a possible 400 unique acyl chains resulting in thousands of possible triglycerides.[1] Critical to the absorption of fat-soluble nutrients from milk is the process of lipid digestion, in which the apolar triglycerides are broken down into monoglycerides and fatty acids. Initial small angle X-ray scattering (SAXS) studies revealed that these amphiphilic milk fat digestion products spontaneously assemble into a progression of liquid crystalline structures over time during *in vitro* lipid digestion, with milk from different species yielding different self-assembled structures.[2,3] This suggests that the structures that form are advantageous for nutrient absorption by each individual species and that controlling liquid crystalline structure formation during digestion is key to nutrient delivery. This presentation will discuss the liquid crystalline structures formed in a variety of milks and milk-like emulsions and the influence of milk processing on the structures that form.[4] The self-assembly of digestion products in adulterated milk will be used to show the sensitivity of self-assembly to lipid composition and relatively simple emulsions prepared from off-the-shelf triglycerides that mimic the digestive behaviour of mammalian milks under digestion will be demonstrated.

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Quantum chemically investigating the origins of Specific Ion Effects

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Despite the ubiquity of specific ion effects among the biological and chemical sciences, our understanding is limited and no quantitative predictive theory is yet available.^[1] Similarly charged ions often influence a system with the magnitude of change following the 130 year old Hofmeister series of cations and anions.^[2] Specifically, the lower critical solution temperature (LCST) of poly(*N*-isopropylacrylamide) (pNIPAM) is dramatically depressed with kosmotropic anions, whereas chaotropic anions have a mild depression or even increase the LCST depending on concentration^[3]. The series order is known to be system dependent, occasionally undergoing series reversals due to such things as solvent, surface, pH, concentration and counterion. The Gibbs free energy of interaction (DG) of NIPAM – cation – anion complexes in various solvents was calculated using Density Functional Theory (M06-2X^[4]/cc-pVDZ^[5]). A monovalent series of cations (Li⁺, Na⁺, K⁺) and anions (F⁻, Cl⁻, NCS⁻) has been investigated in a range of solvents (water, methanol, acetonitrile, DMSO). It was found that DG follows a Hofmeister series independent of the solvent, substrate or counterion; furthermore, accounting for desolvation penalties shows series reversals dependent on the substrate and solvent Lewis acidity (anionic series) and basicity (cationic series).

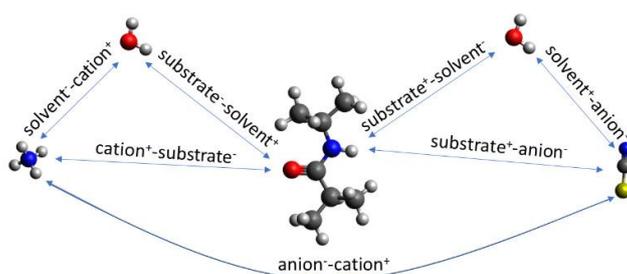


Figure1: Specific ion effects appear to arise from an interplay of competing interactions

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OC011

Specific ion effects in mixed salt environments on a thermoresponsive poly(oligoethylene glycol methacrylate) brush

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Poly(polyethylene glycol methacrylates) (POEGMAs) are thermoresponsive polymers which switch in hydrophobicity at their lower critical solution temperature (LCST).¹ For POEGMAs in the brush regime, this manifests as changes in brush thickness. The swelling/collapsed transition of POEGMA brushes has been shown to be influenced by the concentration and identity of ions present in the system.² Single salt studies on POEGMA brushes show that the transition is shifted to higher temperatures in the presence of chaotropic ions, such as thiocyanate, or to lower temperatures in the presence of kosmotropic ions such as acetate. Limited work exists for systems of salt mixtures as would commonly be found in application environments.³ Recently an investigation on the behaviour of a POEGMA brush in mixed salt environments of potassium acetate and thiocyanate was undertaken. Neutron reflectometry, and quartz crystal microbalance with dissipation have shown that the balance of the influence of the two ions on the structure of the brush is temperature dependent. At low temperatures the influence of the acetate and thiocyanate ions are additive and approximately equal in magnitude. At higher temperatures the influence of the acetate ion diminishes, resulting in an increase in the relative influence of the thiocyanate ion on the brush structure.

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OC012

Colloidal aggregation and gelation used to prepare composite materials with improved mechanical properties

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The preparation of polymer-based composite materials reinforced with inorganic fillers has been the subject of many investigations as well as of technological advancement during the last decades. One of the major challenges is to obtain an optimal dispersion of the filler materials inside the polymer matrix. In this work, we show that a major improvement in the dispersion of nanofillers inside a polymer matrix can be achieved by preparing composite materials from colloidal dispersions of both the polymer and the filler. By working with stable dispersions of colloidal particles, perfect mixing conditions can be achieved, which can be maintained all the way during the drying of the suspension to the final solid composite material. However, our approach is not limited to the simple case of stable colloidal suspensions. Starting from highly concentrated colloidal suspensions of soft poly(butyl acrylate/methyl methacrylate) copolymer particles (80 nm diameter), and using small Ludox silica particles as fillers, we showed that, by controlling the pH of the suspension, it is possible to colloiddally destabilize the silica, inducing first an aggregation, then a gelation of the particles, trapping inside the polymer colloids. The formation of a colloidal gel, which is a percolating structure formed by the filler, leads to the preparation of materials, upon evaporation of water, with improved mechanical properties compared to equivalent materials prepared from stable colloidal dispersions. Ultra-small angle X-ray scattering has been used to confirm the difference in the structure of the filler inside the final material. To confirm the generality of the process, a similar approach has also been used in the case of composite materials made with graphene oxide as inorganic fillers, which lead to the composite materials with improved colloidal properties when aggregation of graphene oxide nanosheets has been induced, before removal of the solvent dispersing the particles.

OC013

Properties and applications of multi-functional lubricin coatings in electrokinetic, sensor, and bionic technologies

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This presentation will highlight recent work investigating and developing multi-functional lubricin coatings for electrochemical applications. Lubricin is a large glycoprotein found in synovial fluids and coating cartilage surfaces in articular joints (knees, hips, etc.). Lubricin has long been recognized as being an important biological boundary lubricant molecule; however, lubricin possesses a number of lesser-known properties that are particularly advantageous to many electrochemical applications. First, lubricin's unique molecular structure leads it to rapidly self-assemble on virtually any substrate into a uniform, well-ordered 'telechelic' polymer brush layer. These lubricin brush layers exhibit impressive anti-adhesive properties comparable to, and in many cases better than, traditional PEG coatings. The lubricin molecule possesses an overabundance of anionic charge, a property that is atypical among antiadhesive molecules, which can be used to drive electrokinetic processes such as electrophoresis and electroosmosis in microfluidic devices. The diffuse structure of the lubricin brush also leads to size selective transport properties which then permits lubricin coated electrodes (or other active interface) to be used to sense and detect small analyte molecules in highly fouling fluids (e.g. blood plasma) with minimal loss in electrochemical activity. Finally, the excellent electrochemical stability, innate biocompatibility, and surface fouling resistance of lubricin has utility as a coating material to control the effects of surface fouling in bionic electrode implants.

Formulating pharmaceutically acceptable non-aqueous microemulsions

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Microemulsions are clear, homogeneous and easy to prepare dispersions of water and oil stabilised by one or more amphiphiles - typically a surfactant and a cosurfactant. Due to their numerous beneficial properties, including long-term stability, clarity and low viscosity, and their ability to solubilize large quantities of hydrophilic and/or lipophilic materials, microemulsions have been studied for their potential as formulation media and encapsulation vehicles in a variety of areas. Nonetheless, few commercial food- and drug-grade microemulsions have been developed over the years, mainly due to the need to use high surfactant concentrations and/or cosurfactants to promote microemulsification, which could decrease the biocompatibility of the systems. To address this issue, this project aims to increase the understanding of the guiding principles behind the formation of pharmaceutically acceptable cosurfactant-free nonaqueous microemulsions, in which the naturally occurring lipid soybean phosphatidylcholine (SPC) is employed as the surfactant and various generally regarded as safe (GRAS) solvents are used. To this end, a range of polar solvents (PSs, used instead of water) and non-polar solvents (NPSs, oils) were employed to systematically study the effect of solvent structure and physico-chemical properties on the phase behaviour, air-solvent interface lipid packing and bulk microstructure of nonaqueous SPC systems. The results of these studies suggest that there are two key structural solvent characteristics that affect the behaviour of the systems: the amphiphilicity of the polar solvent and the molecular volume of the non-polar solvent, which when increased and decreased, respectively, promote increased lipid/solvent interfacial mixing, an increase in the microemulsion (clear) area of existence in the phase diagrams and a transition of the microstructures observed from lamellar to large ellipsoidal to smaller more spherical structures (Figure 1).

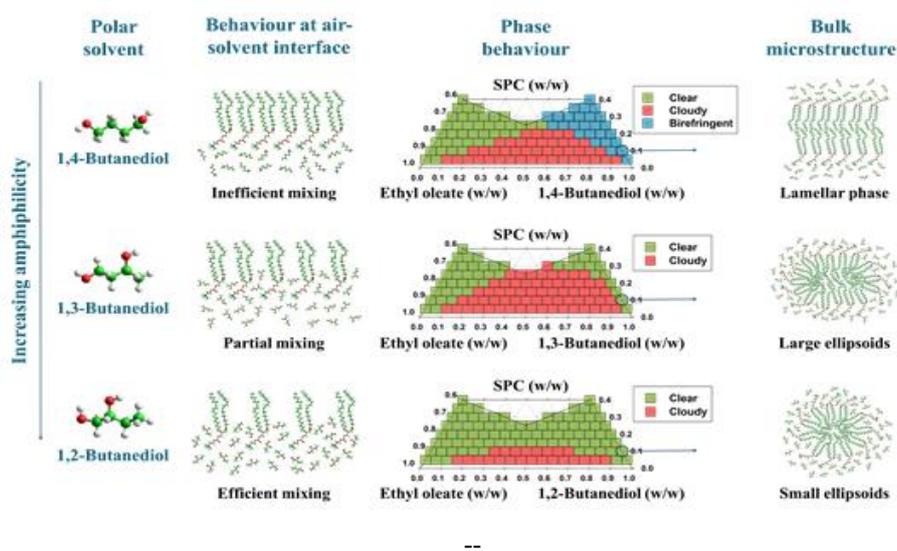


Figure 1. Effect of polar solvent amphiphilicity on lipid interfacial (air/polar solvent) packing, phase behaviour and microstructure in PS/SPC and PS/SPC/PS systems.

OC015

Skin, creams and the ambient from a 3D perspective

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In-depth understanding of skin barrier function and interactions between the skin and specific excipients comprised in topical formulations clearly benefits development of efficacious medications for various skin diseases. Since many formulations are heterogeneous and often contain volatile components (e.g. water) they will inevitably suffer reformulation when applied, leaving a residual film on the skin surface. This may change the thermodynamic activity of the active substance in the residue and affect its permeation across skin. Moreover, film formation may induce occlusion, which subsequently increases skin hydration - a key aspect that changes the physical and mechanical properties of the skin. In the current study we combine among others confocal laser scanning microscopy, synchrotron based X-ray tomography and solid state NMR to gain further understanding on how the physicochemical properties of skin depend on skin topography, formulation residue formation and surface coverage, as well as excipient interactions with skin and effects of ambient humidity and temperature.

OC016

Binary coalescence of drops with bulk and interfacial flows triggered by the presence of surfactant

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What will happen upon merging of miscible drops that have different composition?

Merging of dissimilar drops, being of different size and/or composition is an essential part of multiple promising applications enabling release and mixing of various species in bespoke way. However, till now there is still a lack of understanding of the effect of the various factors involved on the kinetics of coalescence and the rate of mixing of the contents of the drops. Typical investigation of coalescence involves same drops, however merging of dissimilar drops, being of different size and/or composition remains an open question. This study provides a thorough understanding of the merging process immediately after contact of surfactant-laden and surfactant-free aqueous drops in surrounding oils [1, 2]. Numerical simulations provide a deeper insight into the liquid redistribution during the merging and the results are in good agreement with the experimental data. It is observed that the surfactant-free drop intrudes into the surfactant-laden drop in the form of a penetrating jet and mixing patterns within the coalescing drops are due to the force imbalance caused by capillary pressure difference and surfactant-induced Marangoni stresses; the intensity of the convective bulk motion is also influenced by the viscosity of the outer phase.

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OC017

Liquid marbles using electrostatics: Effect of core particle size

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Using electrostatics in the preparation of liquid marbles (LMs) and particle-stabilised aggregates has been recently investigated as an alternative to the conventional method of rolling liquid droplets across a bed of particles¹⁻². Traditionally, only hydrophobic particles can be utilised, as the droplet is stabilised due to their attachment at the air-liquid interface³. Introducing a non-contact technique allows for a greater range of particle hydrophobicities as well as increasing the range of particle and droplet sizes available to successfully form LMs⁴. Here we present results from our polymer particle stabilised droplets using the electrostatic transfer method. Investigations into the influence of applied potential and particle size were completed by bringing an earthed 5 μ L water drop into the vicinity of a bed of highly charged polystyrene particles with diameters between 22 and 149 μ m. A range of applied potentials allowed for the successful electrostatic transfer of particles to the pendent water droplet resulting in particle-liquid aggregates. LMs stabilised with hydrophobic polypyrrole coated polystyrene core-shell particles across a similar size range were formed using the same route. The impact of the high conductivity of the surface of these particles will be discussed.

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OC018

Clofazimine flash nanoprecipitated nanoparticle formulations for the treatment of cryptosporidiosis

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Clofazimine has recently been identified as a potential new drug for the treatment of cryptosporidiosis.¹ Fast-acting treatment of the infection is required to limit dehydration and malnutrition that can lead to diarrhoeal deaths. As the commercially available clofazimine formulation, Lamprene[®], suffers from high inter- and intra-subject variability in the drug exposures due to dissolution-limited absorption,² re-formulation of clofazimine is desirable. Development of clofazimine nanoparticles through the process of flash nanoprecipitation (FNP) has been previously shown to provide faster drug dissolution rates compared to clofazimine crystals and Lamprene[®].^{3,4} Herein, we investigate the effects of lipids (in milk and infant formula) under digestion on the in vitro solubilisation behaviours of lecithin-, zein- and casein-stabilised nanoparticles prepared by FNP since consumption of food was recommended following the intake of clofazimine. The SAXS/WAXS beamline at the Australian Synchrotron was used to monitor changes in the intensity of diffraction peaks from crystalline drug during digestion to track drug solubilisation and polymorphic transformation. Our results strongly suggest that clofazimine nanoparticles prepared by FNP exhibit faster solubilisation during digestion that is dependent on the lipid content and may therefore be highly suitable as an excipient in the treatment of cryptosporidiosis where fast onset of action in the intestinal milieu is required.

OC019

Raspberry Particles in Paint?: Film-forming Latexes prepared by Pickering Emulsion Polymerisation

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Polymer latex particles of diameter <300 nm have been prepared in the absence of surfactants through a Pickering-type emulsion polymerisation process stabilised in part by silica nanoparticles.¹ Control of the silica wettability through modulation of reaction pH or by reaction of the nanoparticles with a hydrophobic silane resulted in silica-covered latex particles. Conditions were investigated to maximise adsorption of nanoparticles onto the surface of the latex such that the resultant latex was completely armoured in nano-silica. The oil-in-water emulsion polymerisation process used methyl methacrylate (MMA) and n-butyl acrylate (BA) as co-monomers, along with a water-soluble initiator, in the presence of a commercially available colloidal nano-silica (Ludox[®]- TM40). It was found that precise pH control before polymerisation using methacrylic acid (MAA) facilitated the formation of armoured latexes, and mechanistic features of this process are discussed. An alternate method of the preparation of these latexes were identified whereby the addition of vinyltriethoxysilane (VTES) to control wettability readily resulted in latexes completely armoured in colloidal nano-silica (Fig.1). The latexes were characterised using SEM, cryo-TEM and AFM imaging techniques and the mechanism behind the adsorption was investigated through surface pressure and contact angle measurements in order to understand the factors that influence this irreversible adsorption. Results indicate that nanoparticle attachment (but intriguingly not latex size) is dependent on particle wettability, providing new insight into the formation of nanoparticle-armoured latexes, along with opportunities for further development of diversely functionalized inorganic/organic polymer composite particles.

OC020

High throughput and machine learning approaches to characterising stoichiometric and non-stoichiometric protic ionic liquid-water solutions

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Protic ionic liquids (PILs) are cost efficient “designer” solvents which can be tailored to have properties suitable for a broad range of applications. The vast number of possible cation and anion combinations of protic ionic liquids, along with additions of co-solvents and solutes makes it difficult and time-consuming to optimise them for specific desired properties. Here we have used high throughput methodologies which enable rapid synthesis, characterisation and analysis to explore an extensive range of PIL containing solvents. A selection of aqueous non-stoichiometric PILs were prepared through additions of the corresponding precursor acid or base and water. A latin hypercube sampling method was used to select 25 compositions for each non-stoichiometric PIL, covering the composition space. The liquid nanostructure and surface tension was obtained for each sample, along with the apparent pH, where there was considerable water present. Two machine learning methods, multiple linear regression and artificial neural networks, were applied to the data to determine the effect of different cation and anion structural features, non-stoichiometry and water for these systems, and to enable property prediction of a broader range of solvents. This has enabled structure-property relationships to be developed for a multivariate sample space for PIL containing solutions. This methodology is useable for developing solvent systems containing multiple species, such as one or more ILs with co-solvents

OC021

Nanostructure of the deep eutectic solvent / platinum electrode interface as a function of potential and water content

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The interfacial nanostructure of the three most widely-studied Deep Eutectic Solvents (DESs), choline chloride:urea (ChCl:Urea), choline chloride:ethylene glycol (ChCl:EG), and choline chloride:glycerol (ChCl:Gly) at a Pt(111) electrode has been studied as a function of applied potential and water content up to 50 wt%. Contact mode atomic force microscope (AFM) force-distance curves reveal that for all three DESs, addition of water increases interfacial nanostructure up to ~40 wt%, after which it decreases. This differs starkly from ionic liquids, where addition of small amounts of water rapidly decreases interfacial nanostructure. For the pure DESs, only one interfacial layer is measured at OCP at 0.5 nm, which increases to 3 to 6 layers extending ~ 5 nm from the surface at 40 or 50 wt% water. Application of a potential of ± 0.25 V to the Pt electrode for the pure DESs increases the number of near surface layers to 3. However, when water is present the applied potential attenuates the steps in the force curve, which are replaced by a short-range exponential decay. This change was most pronounced for ChCl:EG with 30 wt% or 50 wt% water, so this system was probed using cyclic voltammetry, which confirms the interfacial nanostructure is akin to a salt solution.

OC022

Universal Nano-Lithographic Technique for Different Shaped Functional Anisotropic Nanoparticles

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Functional anisotropic nanoparticles have potential to significantly affect the performance of coatings. The size, shape and the functionality associated with the material of the anisotropic nanoparticles can modify and enhance the properties of the coatings. The application of anisotropic nanoparticles in functional coatings interested us to develop a flexible method for fabricating anisotropic nanoparticles of varying size, shapes and materials of interest. The aim of this work was to establish a universal method for making different shaped anisotropic nanoparticles, such as cubes, disks, cylinders and to choose the functional materials as required in the coating applications. This was done by following a template directed approach. The most advanced and dedicated thermal scanning probe lithographic instrument, NanoFrazor, was combined with dry etching step to make templates of different shaped patterns according to the cross-sectional geometry of final nanoparticles. Electron beam deposition of different metal/metal oxides (silica, titania, silver) onto the templates allowed us to be flexible with the selection of nano-materials. To evaluate the potential of a number of these particles to be incorporated into coatings, solution based characterisation of these particles for properties such as zeta potential will also be discussed.

Uniquely shaped polymer colloids via liquid crystal templating

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Shape and deformability are important properties of polymeric colloids, as both play a crucial role *in vivo* behaviour. For example, softer particles have longer circulation times and lower splenic accumulation,¹ while tunable shape and elasticity have an effect on cell uptake and cell trafficking.² Our previous work on precise shape control of liquid crystalline particles used cubosomes and hexosomes to produce particles with unique faceted and rotational symmetry,³ but were not stable against some chemical and enzymatic conditions. Here we use self-assembled lyotropic colloids as templates for polymerization to form more resilient shaped particles in order to expand their applications. In this work, cubosomes and hexosomes are prepared using bottom-up and top-down methods with inclusion of photo-initiators. After soaking particles in the monomer solutions, the cross-linker and monomers diffuse inside the particles without affecting their shapes. Photopolymerization transforms the self-assembled structures into strongly bonded networks. The polymerized particles preserve their shapes after removal of the lipid template, and deform elastically when subjected to external forces. Particle size and shape can be controlled by varying template phase, and formation process, and elasticity can be tuned by monomer choice. Shaped soft polymeric particles could act as novel carriers for actives in cosmetic, food, and biomedical applications.

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OC024

Composite ink development from bioceramic nanoparticles for bone tissue regeneration

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Bioprinting has been used to deposit living cells, hydrogels (3D-ink) and other biomaterials in user-defined patterns to build complex tissue constructs “as a bottom up approach.”[1] Our goal in this study was to study the formation of homogenous composite ink developed from degradable bioceramic nanoparticles. The printed construct containing ion releasing ceramic particle will be safe, easy to manipulate, and effective in inducing bone formation. The 3D-printable particles reinforced ink can be used to create a robust composite scaffold that not only promotes bone regeneration, but also has elastic mechanical properties that improves functionality and delivery in both open and minimally invasive procedures. We synthesized the forsterite particles using sol-gel technique [2] with 30-40 nm size and evaluated 3D-printing of a composite ink that incorporates nanoparticles of forsterite (nFo) with different concentrations into the two different 3D-ink with various crosslinking systems: 1) pure alginate (AA), 2) methacrylated alginate (AA-MA). The result showed by controlled crosslinking, optimized amount of particles 0.3 wt%, and adjusting the pressure and feeding rate in 3D printing technique, high resolution and homogenous nFo-AA or nFo-AA-MA printed structure is achievable and we believe this is the basis for a highly effective bone graft substitute as it shows high bioactivity and degradation.

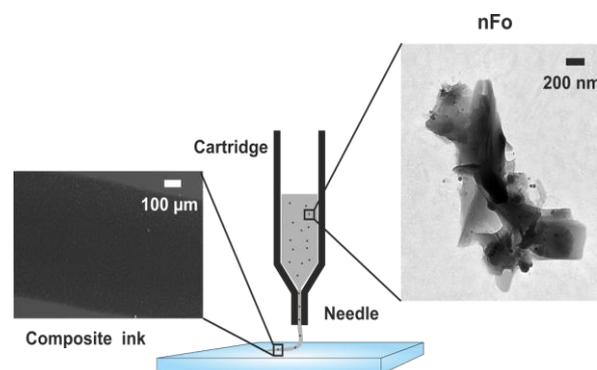
In conclusion, this study demonstrates optimization of material parameters for 3D printing of nFo-AA scaffolds and enhancement of mechanical properties and bioactivity by incorporation of forsterite particles.

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Acknowledgment

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3D printing forsterite composite ink

Designing food colloidal systems using microstructure engineering approach

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The WHO in its Global Status Report on non-communicable diseases from 2014 warned that worldwide obesity levels had nearly doubled since 1980 and due to the concern surrounding this figure, one of the main global targets is to half this number by 2020.

It has been agreed that the best way to reach this goal is to promote physical activity and consumption of a healthy diet. Therefore, principal route to obtain more of healthy and nutritious food is to decrease the amounts of fat, sugar or salt in existing food products.

Many commercial food products have colloidal microstructure. Their texture and mouthfeel are important contributors to the eating experience and play a significant role in consumer perception and acceptance of a food product. However, due to the complexity of colloidal food systems, successful reformulation without affecting product texture or mouthfeel is a challenging task. Microstructure engineering approach enables understanding of mechanisms governing colloidal food systems formation and successful reformulated product design.

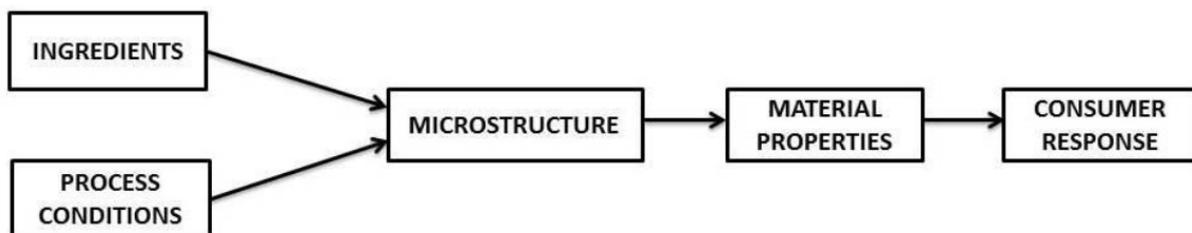


Figure 1 Microstructure engineering approach to colloids food systems design

OC026

Dynamic graphene oxide network enables spray printing of colloidal gels for high-performance micro-supercapacitors

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Properly controlling the rheological properties of nanoparticle inks is crucial to their printability. Here we report that colloidal gels containing a dynamic network of graphene oxide (GO) sheets can display unusual rheological properties after high-rate shearing. When mixed with polyaniline (PANI)nanofiber dispersions, the GO network not only facilitates the gelation process but also serves as an effective energy transmission network to allow fast structural recovery after the gel is deformed by high-speed shearing. This extraordinary fast recovery phenomenon has made it possible to use the conventional air-brush spray technique to print the gel with high-throughput and high fidelity on non-planar flexible surfaces. The as-printed microsupercapacitors exhibit an areal capacitance of 5~8 times higher than the traditionally spray-printed ones. This work highlights the hidden potential of two-dimensional materials as functional yet highly efficient rheological enhancer to facilitate industrial processing of nanomaterial-based devices.

OC027

Efficient room-temperature production of high-quality graphene by introducing removable oxygen functional groups to precursor

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Excellent solution-processability of graphene oxide (GO) have provided a collection of strategies for the construction of functional graphene assemblies. To improve the performance of graphene-based materials, structurally intact GO should be prepared as the precursor of high-quality graphene; however, the solution chemical methods were constantly challenged by the trade-off between structural integrity and fabrication yield. Here, we report a wet chemical method for the high-efficient production of high-quality graphene oxide precursor with all steps operated under room-temperature. Functionalization of graphite was performed with the control of temperature and water content in concentrated sulfuric acid-potassium permanganate system and the resulting GO showed monolayer yield over 120 %. We show that the increased production yield comes from the high functionalized degree and, more interestingly, the functional groups on GO were proved to be removable upon reducing with hydroiodic acid, which produced high-quality graphene-based materials (for chemically reduced GO films, the conductivity could reach 780 S cm^{-1}). The good solution processability of GO synthesized herein enables the successful fabrication of thin films, fibres and ultralight aerogels. Furthermore, the presented approach is quite energy-saving, which could meet the requirements for scalable production of graphene in industry.

OC028

Improved rheology and high-temperature stability of hydrolysed polyacrylamide by using graphene oxide nanosheet

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Hydrolysed polyacrylamide is a polymer that extensively used in chemical industry and hydrocarbon extraction and refinery processes, but suffers a common problem of high-temperature instability. This study improved high-temperature rheological characteristics of hydrolysed polyacrylamide (HPAM) by using novel graphene oxide (GO) nanosheets. Stable GO dispersions in aqueous HPAM were formulated, and their dynamic and viscoelastic behaviours were studied. The results showed that the addition of GO significantly increased the viscosities and high-temperature stability of the base polymer fluid, as well as the elastic properties of the dispersion. Spectral data indicated the formation of covalent linkages and electrostatic hydrogen bonding between the GO and the HPAM functional groups and reinforce the HPAM structure by two-dimensional (2D) layer of the GO particle, leading to enhanced stability and viscosity that is beneficial for high-temperature oil recovery.

Ligand-mediated interaction between colloidal nanoparticles

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Metal and semiconductor nanoparticles (NPs) exhibit unique properties that enable their use in a wide range of technological applications. In order to prevent them from randomly aggregating in solution, stabilizing agents are often attached to the NPs surface. Experiments [2] and simulations [3,4] indicate that NP stability and assembly are strongly dependent on how ligands order on their surface. We use SAXS to study the temperature-dependent colloidal stability of gold NPs in alkane solution and compare the results with MD studies of the ligand order and the interaction potential between pairs of particles. Our results indicate that the interaction between gold NPs in solution is markedly affected by the structure of the ligand shell, changing from repulsive to attractive as the ligands align with one another to form ordered bundles. Therefore, the stability of these particles can be predicted by controlling factors that change the ordering of the ligands, such as core size and ligand length. Changes on the structure of the ligand shell are not accounted by existing theories such as Flory-Huggins solution theory, which may explain why they often fail to predict the stability of such systems and shows the need for improved models that include them.

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OC031

Characterization of surface properties of nano- and microparticles by Hansen parameters to predict particle-particle and particle liquid interaction

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Surface properties are crucial for dispersion process of powders and agglomerated/aggregated disperse phases, e.g. pigments, catalyzers and carbon black, and key for many industrial applications. Dispersibility and the resulting quality of dispersion are determined by several factors including quality of continuous phase, kind and especially surface structure of raw materials, dispersion process and additives. A priori, such processed disperse systems are thermodynamically unstable. This talk focuses on surface properties of solid particles. Ability (easiness) to get dispersed is characterized by the Hansen concept of "Like dissolves Like". It starts from Hildebrandt solubility parameter (square root of cohesive energy between molecules, related to vaporization) but subdivided into three contributions, namely disperse, polar and Hydrogen-bond to account for the different kinds of interaction between a particle and solute molecules. Basically, particles are dispersed into different liquids of 3D-Hansen space. Based on their behavior - good or bad dispersibility – liquids are ranked as "Good" or "Bad" and dispersion, polar-polar and hydrogen-bonding parameter for the particle under consideration calculated. We describe experimental procedures for automatic determination of Hansen parameters of particle surfaces based on normalized sedimentation velocity by analytical centrifugation (STEP-Technology®, LUMiSizer®, LUMiReader) based on normalized sedimentation velocity [1, 2]. We discuss experimental results and Hansen Parameters obtained by profiling plain particles (pigments, Carbon Black, ZnO-quantum dots and CNT) as well as surface modified/decorated ones. It was also shown, that, as theoretical predicted, mixing two bad liquids may result in a good liquid. Furthermore, in case of Carbon Black dispersion process (type and energy intensity) itself changes polar-polar as well as hydrogen-bonding interaction parameters but not the dispersion contribution. In summary, Hansen parameters of particle surfaces can be calculated based on experimentally obtained normalized relative sedimentation time (instrumental approach). These parameters allow to predict dispersibility into different matrices.

OC032

Colloidal stability of apolar nanoparticles: effect of ligand and solvent structure

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Being able to predict and tune the colloidal stability of nanoparticles is essential for a wide range of applications, yet our ability to do so is poor due to a lack of understanding of how nanoparticles interact with one another [1]. The organic ligand shell that coats most inorganic nanoparticles dispersed in apolar solvents is essential for keeping the particles from randomly aggregating in solution, but can affect the particle stability in subtle and surprising ways. In particular, the ligands can undergo a temperature-dependent order-disorder transition in solution (see figure) that switches the particle-particle interaction from repulsive to attractive [2-4]. As we have shown, the temperature of this transition is sensitive to a range of factors, including the particle dimensions, density of ligand coverage, and ligand length, often leading to non-linear trends that cannot be explained using conventional colloid theory. In this work, we show that changes in the ligand and solvent structure can also strongly impact the transition, and explain (i) how a single methyl group on a ligand can increase particle solubility by three orders of magnitude [5] and (ii) how particles can have dramatically different interactions in solvents with the same Hamaker constant. Our results for Au and CdSe nanoparticles, obtained from SAXS experiments and molecular dynamics simulations, provide a microscopic description of the forces that determine the colloidal stability of apolar nanoparticles and explain why classical colloid theory fails.

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OC033

Specific ion modulated thermoresponse of PNIPAM brushes

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The internal structure of thermo-responsive poly(N-isopropylacrylamide) (PNIPAM) brush coatings has been investigated via small angle neutron scattering for colloidal silica substrates,[1] and neutron reflectometry for planar substrates.[2] When tethered to a surface in the polymer brush regime, the normally abrupt PNIPAM lower critical solution temperature broadens into a temperature transition range spanning up to 20 degrees.[3] The use of neutrons to interrogate these systems, has enabled subtle variation in the brush volume fraction profile normal to the substrate to be elucidated. The internal structure of the PNIPAM brush on both colloidal and planar silica substrates showed a swollen brush at low temperatures (18 and 25 °C) which decayed exponentially away from the substrate while a collapsed block like conformation with 60% polymer volume fraction was present at 40 °C. Vertical phase separation was evident at intermediate temperature (30 and 32.5 °C).[1] Complementary rheological measurements on the colloidal brushes as a function of temperature were interpreted on the basis of this knowledge of the brush depth profile. A particular focus of our attention has been the modulation of the polymer brush thermoresponse in the presence of specific ions, with kosmotropic ions reducing the brush collapse temperature with increasing ionic strength and chaotropic ions initially increasing the brush collapse temperature.[1-4]

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OC034

Heavy molecules from the national deuteration facility for application within colloidal and interfacial sciences

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The molecular deuteration of organic compounds is an essential prerequisite in many spectroscopic and scattering studies, including NMR and IR spectroscopic methods, and in neutron scattering and reflectometry experiments. The need for deuterated molecules is critical and diverse in application, yet despite this need there have been limited global initiatives in the field of molecular deuteration. Those programs that do currently exist primarily focus on the biological deuteration of proteins and lipids, while those molecules commonly used in the interfacial and colloidal sciences are absent within the deuterated molecule catalogue. This has resulted in a restriction of the detailed experiments that can be performed bringing about a bottle-neck for advancement in these areas.

This paper will detail the recent advances and the impact of the bespoke deuterated compounds produced by the National Deuteration Facility at ANSTO for the colloidal and interfacial science community. Key investigations will be discussed that reveal the exciting and diverse characterisation studies which are now available as a result of these custom deuterated molecules. The applications from recent high-impact case studies will be described along with the synthesis of new deuterated molecules which are unavailable from commercial sources. Such molecules to be discussed include deuterated cholesterol, phospholipids and glycerides with deuterated oleyl chains, deuterated phytantriol, and a number of deuterated ionic liquids. These molecules have been used to investigate complex nanoscale systems in the field of interfacial and colloidal science, specifically in areas such as drug delivery, food technology and in 2D light harvesting networks using a number of spectroscopic and scattering techniques.

OC035

What do surfactants do at the oil/water interface?

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Industrial formulations commonly use more than one stabiliser, but different combinations of polymeric, anionic, cationic and non-ionic surfactants may act antagonistically to each other and not stabilise the interface as well as intended. A typical hair conditioner formulation, for example, may contain low molecular weight poly(dimethyl siloxane), PDMS oil, emulsified by polymeric surfactants (such as Pluronic F127) in a buffer solution; at point of use, it can be subjected to significant dilution and be brought into contact with further surfactants. The complex interactions between the polymers, surfactants and the electrolytes at the interface will affect the performance of the final product. We have developed a covalently anchored PDMS film as an immobilised oil layer to study the structures of Pluronic F127 adsorbed at the oil/water interface. Results from neutron reflection and QCM show that F127 forms a loosely packed thin layer at the PDMS/water interface, while addition of SDS and CTAB causes desorption of F127 from the interface. Low concentrations of SDS are seen to partially clean the surface of F127 while high concentrations of surfactants form a mixed layer at the interface. The effect of salt on the adsorption behaviour was also investigated; both UV-Vis absorbance and QCM studies showed addition of different sodium halide salts leads to dehydration and collapse of the adsorbed F127 layer and that the effect is larger for more kosmotropic anions. These results offer formulation rules that link self-assembly behaviour and structural measurements through to the performance of the industrial formulation.

OC036

Understanding interfaces in organic optoelectronic devices using neutron and x-ray scattering

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Organic optoelectronic devices such as organic light emitting diodes (OLEDs), solar cells and sensors are normally multilayer structures with each layer performing a specific function. In such devices, the structure of the interfaces between the layers and diffusion of materials at those interfaces are critical characteristics.

In the case of OLEDs, diffusion can lead to intermixing of the various layers, such as the active layer and charge transport layers. Such intermixing causes degradation in performance and so materials need to be chosen to minimize diffusion, particularly at elevated temperatures. For organic solar cells, on the other hand, diffusion of one organic material into another to form a bulk heterojunction is essential for good performance. Devices are typically annealed to ensure that the appropriate structures are formed and again materials choice is critical. Finally, fluorescent sensors rely on the diffusion of an organic analyte, such as an explosive material, through the film of sensing material to quench fluorescence and lead to a sensitive signal. For a reusable sensor it is desirable to have controlled diffusion so that the analyte can be removed when desired to enable subsequent sensing events.

Neutron reflectometry (NR) is a powerful technique for observing diffusion in organic materials, allowing the sensitive real-time determination of the layer structure in films of similar organic materials and the changes that occur during diffusion. Over several years our group in the Centre for Organic Photonics and Electronics (COPE) has studied the effect of diffusion on the structures and performance of each of the above types of devices and we are now in a position to begin to understand the relationships between molecular structures, diffusion and device performance.

OC037

An improved depolarized dynamic light scattering method to calculate translational and rotational diffusion coefficients of nanorods

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Depolarized dynamic light scattering (DDLS) has the potential to determine size, aspect ratio and rotational diffusion coefficients of nanorods. However, to date the technique has not been widely used, due to ambiguity in the interpretation of the experimental data [1]. There are several problems: first, it is unclear over which range of scattering angles each theory may be valid; second, the interpretation is complicated by the low depolarized signal; and third, the effect of the angular dependent translational rotational coupling is difficult to gauge [2]. To date there has been no systematic experimental study of these effects. In this article we address this by describing a method for determining the appropriate range of scattering angles, allowing the unambiguous determination of the translational and rotational diffusion coefficients of rod like particles.

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OC038

Quantifying the dynamic and equilibrium interactions of confined anisotropic nanoparticles

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We discuss a new technique for measuring the 3D position and orientation of individual anisotropic nanoparticles (e.g. Janus particles, ZnO nanorods and carbon nanotubes) diffusing near a confining liquid interface. Conventional tools are limited by the existence of particle anisotropy and the proximity of an interface, and fundamentally incapable of providing the spatiotemporal resolution required to capture translational and rotational dynamics. With our new technique we are able to measure position and orientation at millisecond time-intervals, enabling us to quantify diffusion in each spatial mode as a function of particle-interface separation. These same data can also be used to measure equilibrium interaction potentials with orientation and position effects decoupled, completing a rich set of tools for probing anisotropic interactions relevant to the study of self-assembly and transport phenomena. We discuss results obtained for systems of ZnO nanorods and carbon nanotubes diffusing in aqueous solutions in order to demonstrate the physical insights enabled by this new technique. Aside from fundamental applications, this technique will be particularly useful for understanding and tuning the self-assembly of films and other structures incorporating anisotropic nanoparticles.

Emergent properties of Janus spheres: experiments

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In recent years, clusters of Janus particles have emerged as a new division of colloidal structures. Janus spheres have two distinct hemispheres [1], an asymmetry contributing towards interesting emergent structures when they aggregate. Our interest in the emergent properties of Janus spheres is driven by two factors. Firstly, there are untested simulation results suggesting that Janus particle clusters can form interesting phases [2]. Secondly, the asymmetry of Janus spheres suggests that the aggregation process could be controlled. One potential mechanism for controlling self-assembly involves the self-orientation of Janus spheres in flow. This is the subject of our current research relating to the dynamics of individual Janus spheres with slip boundary conditions [1]. In preliminary experiments, free diffusion studies have been conducted to measure the diffusion coefficients of 800 nm and 600 nm diameter silica spheres. Control silica spheres were compared with hydrophobic (silane coated) silica spheres (see Figure). Initial results have indicated there was no detectable difference between the diffusivity of control and silane coated silica beads. Further experimental studies are required to establish whether slip-induced dynamics can be used to control the clustering behavior of Janus spheres. The overall goal is to develop and study assemblies of asymmetric Janus spheres which have novel and/or interesting emergent properties, that is, macroscopic physical properties. This will be achieved by controlled fabrication of interesting micro- and nano- scale Janus spheres, and by careful study of their aggregation using microfluidics.

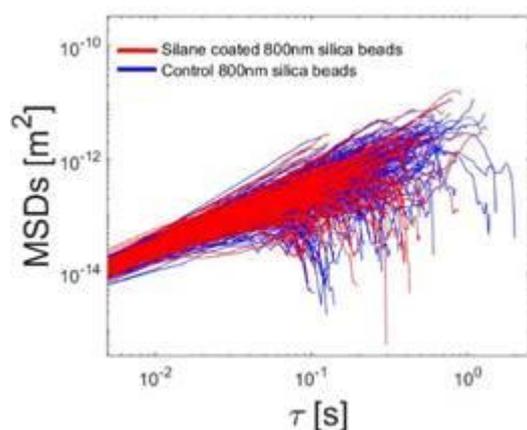


Figure: Mean square displacements (MSDs) as a function of time for 800nm silica spheres

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OC040

Nanoparticles self-assembly for the preparation of bioinspired materials with stimuli-responsive color changing ability

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Octopuses and cuttlefish possess some of the most amazing camouflage abilities of the entire animal kingdom. The core of the camouflage mechanism lies in chromatophores, which are special cells with the ability to displace pigments, located in small pockets in the middle of the cell, over a much larger surface, thus enabling the overall appearance of the cell to change from white or transparent to the specific color of the pigment. Inspired by this mechanism, we have designed color changing polymeric materials exploiting the self-assembly of responsive colloids. The design of the material, unique in its kind, is based on the incorporation of water droplets, generated by microfluidics, in which magnetic nanoclusters are well dispersed, and impart a brown color to the droplets. These droplets play the same role as chromatophores in the octopus's skin. However, upon exposure to a magnetic field gradient, the clusters rapidly self-organize, align in the direction of the field or accumulate in a small region of the droplet, towards the direction of the strongest magnetic field gradient, thus mimicking the pigment dislocation in the chromatophores. In this manner, the overall color of the droplets changes from dark brown to almost transparent, and leads to macroscopic change in the overall color of the material. To the best of our knowledge, this is the first example of a material with magnetically responsive color change mimicking the pigment dislocation effect.

OC041

Significance of non-DLVO attractions in coalescence of bubbles in salt solutions

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Foam formation and stability is controlled by drainage caused by gravity, coarsening caused by the gas transfer between bubbles, and bubble coalescence caused by thinning and rupture of liquid films between bubbles. Some salts can enhance foam formation by inhibiting bubble coalescence above a critical salt concentration called the transition concentration (TC).

The available models to predict salt TC were developed based on the effects of the Gibbs-Marangoni stress and DLVO attractions (either the London-van der Waals or Casimir-van der Waals attraction). These models failed to predict the TC correctly and significantly underestimate the TC.

This work develops a mathematical model to predict the salt TC and rupture thickness of the saline liquid films between two bubbles. The modelling results are validated by comparing the model's predicted TCs with the experimental TCs from this work and literature. Thin liquid film interferometry is used in this work to determine the TC of halide salt (NaF, NaCl, LiCl, KCl, NaBr and NaI).

Our modelling and experimental results for a single liquid film between two bubbles highlights the importance of non-DLVO attractions in the inhibiting effect of salts on bubble coalescence. The role of soluble gases in non-DLVO is also demonstrated. The results indicate that a lower concentration of soluble gas in salt solutions leads to a decrease in non-DLVO attractions.

OC042

Stability of liquid-infused surfaces in microchannels under pressure-driven fluid flow

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Liquid-infused surfaces exhibit technologically attractive features, such as omniphobicity, antifouling, and drag reducing properties. These attributes are very attractive for microfluidic applications in biomedical devices, pharmaceutical and life science research, micro reaction technology and analytical devices. However, the potential depletion of the infused lubricant could interfere with their practical application. Exposed to external pressure-driven flow, the lubricant can be drained due to shear stress or pressure gradient. The complete depletion of lubricant could suppress the benefits of the infused surface and bring undesired effects, such as clogging of microchannels and microvalves or cross-contamination with the lubricant of the device and the external fluid. In this research, we have created a versatile microfluidic platform for testing the stability of the different liquid-infused surfaces under a range of flow rates and pressure gradients of the external fluid. We test extensively the stability of silicon oil-infused nanowrinkled surfaces,^{1,2} as well as other commercially available substrates. The effect of the fluid flow rate and pressure on the lubricant film is quantified by means of lubricant loss from the surface and drag reduction along the microchannel. The results of this improve our understanding of the failure mechanisms and stability of liquid-infused surfaces in microchannels, thus enabling their application in a more reliable manner as drag-reducing and anti-fouling coatings.

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OC043

Wet stain kinetics for paper based bio-diagnostics

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Paper based diagnostics can offer significant advantages over traditional microfluidic devices. This is due to their low manufacturing cost and relative simplicity that means they can be operated by untrained individuals outside of a lab setting. Although several products are currently in production, much of their design has been optimized by trial and error. This is because the wicking process, and particularly radial wicking from a finite source, is poorly understood and no realistic model has been achieved. Our past research (Hertaeg et al., 2018) has shown that stain analysis on paper is highly reproducible and sensitive, and could be the basis of a new generation of robust bio diagnostic techniques. This research now focusses on the wet area kinetics after a drop is deposited on paper and the subsequent inference of fluid/cell/other constituent distribution. This will allow diagnostics to go beyond equilibrium stain analysis to analysing the formation process, which will reduce the time that tests take to just a few seconds and allows for several new methods of analysis based on the identifiable characteristics of the pre-equilibrium stain kinetics. Particular emphasis is placed on the transitions in wet area growth rate as the dominant mechanisms changes during the process and how these are related to the changes in the interfacial energies and pore morphology between different fluids and substrates.

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OC044

Droplet motion on superhydrophobic surfaces

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The surfaces of many plant leaves are superhydrophobic, a property that may have evolved to help keep the leaves clean by encouraging the beading and rolling of water droplets. While the rolling motion of droplets on superhydrophobic surfaces with conventional slip lengths has been investigated and observed experimentally, the existence of slip-dominated regimes on surfaces with sufficiently high slip-lengths remains relatively unexplored.

In this paper, molecular dynamics simulations are used to investigate the roles of droplet size and surface geometry on the subsequent equilibrium velocity of droplets travelling down superhydrophobic surfaces. The results are examined using an extension of previous theoretical descriptions¹ of droplet motion on surfaces, where an effective slip condition² is applied at the liquid-surface interface. This approach yields three limiting cases for the steady-state velocity of the droplets, where energy losses are dominated by viscous dissipation, surface friction or contact line friction respectively.

We find that in molecular dynamics simulations of droplets on ideal superhydrophobic surfaces with large effective slip lengths, contact line dissipation associated with surface features dominates droplet motion, with droplet velocity increasing with radius. At droplet radii larger than the capillary length, we retrieve the usual viscosity-dominated motion. However, on real leaves, droplet motion is likely to be dominated by viscous shear, and slip, for the most part, can be neglected.

We also consider the movement of droplets across a surface that has controlled wettability that can be varied in time. Simulations of droplets on a surface with a moving wettability gradient show that there exists a maximum velocity above which the droplet cannot keep up with the moving field. Simulation results are presented along with a supporting mathematical model. We discuss the implications of our results for the design of droplet manipulation, microfluidic mixers and lab-on-a-chip devices using switchable surfaces.

Stability of hard-core/soft-shell colloids at different packing fractions probed by light, X-ray and neutron scattering

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Colloids with hard and functional nanoparticle cores and soft polymer shells are versatile building blocks for functional materials design.[1] Crucial for their phase behaviour and functionality are core type, core-to-shell size ratio as well as shell softness. The form factor of the core/shell particles and the density profiles of the soft shells are accessible via SAXS and SANS.[2]

At liquid interfaces strong adsorption occurs and, because of attractive interactions, aggregation is found already at low packing fractions.[3] This can be used to fabricate highly ordered monolayers with defined structures. In contrast the particles are stable in bulk even at very high packing fractions exceeding the hard-sphere limit due to a soft repulsive interaction.[4]

We prepared cm-sized soft photonic crystals from core/shell colloids with absorbing gold nanocrystal cores and systematically studied the crystal structure and diffractive properties. As non-absorbing references, we prepared pitted particles by dissolution of the nanocrystal cores.[5] The resulting purely organic microgels allowed for a direct comparison of structural and optical properties. Dynamic and static light scattering as well as SANS were used to study the core/shell and pitted particles in the dilute state on different length scales. The crystal structure of samples at high volume fractions was analysed by SANS. Independent on the presence or absence of the gold cores, we found fcc crystal structures with pronounced Bragg peaks of several orders. We identify the role of small absorbing nanocrystal cores in soft photonic crystals and show options to alter the photonic behavior of such crystals in future studies.

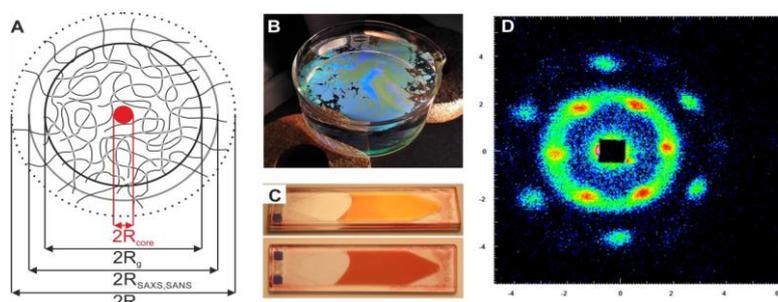


Figure 1: A) Schematic depiction of core/shell colloids with the respective length scales accessible through different scattering methods. Optical appearance at high packing fractions at air/water interfaces (B) and in bulk (C). D) 2D SANS pattern from a colloidal crystal of core/shell colloids.

Acknowledgments:

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OC046

Thermodynamic and kinetic consideration of the micelles with the discrete aggregation numbers and mono-dispersity

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Calix[4]arene-derivative surfactants form monodisperse micelles with a well defined aggregation number (N_{agg}), the value of which is selected from among 4, 6, 8, 12, and 20, corresponding to the Platonic solids. This feature is in strong contrast to conventional micelles. Here, we focused on a kinetics; a transition from dodecamer ($N_{agg} = 12$) to icosamer ($N_{agg} = 20$) induced by a rapid increase of the NaCl concentration (C_{NaCl}) using a stopped-flow device was directly observed with time-resolved small-angle X-ray scattering. N_{agg} was unchanged during 60 s after C_{NaCl} increased, and then abruptly increased to 20. This phenomenon is similar to the phase transitions in a supersaturated or supercooled state, or highly cooperative phenomena. The phenomena may be related to our hypothesis that only a few N_{agg} values are thermodynamically allowed, when N_{agg} is sufficiently small. This is the first observation of such abnormal discontinuous change in micellar aggregation behavior.

OC047

Aggregation kinetics quantified on single biofunctionalized particle dimers reveals heterogeneity in particle surface reactivity

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The colloidal stability of biofunctionalized particles is key for biomedical applications such as drug delivery and biosensing. The complexity of blood plasma tends to stimulate undesired particle aggregation and fuels research on antifouling coatings. However, methodologies to measure, modulate and model the interaction between individual particles are scarce. Here we demonstrate two new techniques to measure and quantify aggregation kinetics: a single dimer experiment and an ensemble experiment. In the single dimer experiment [1], two particles are magnetically confined and the trajectory that a particle follows on the surface of another particle is recorded as a function of time. The experiment reveals spatial heterogeneities of particle surface reactivity, by correlating individual binding events to dimer orientations. In addition we describe an optomagnetic cluster experiment [2] in which particle dimers are induced by a magnetic field and detected by light scattering. The rotating magnetic field modulates the light scattering intensity and allows rapid quantification of aggregation rates. By the careful design of measure and actuation protocols we are able to quantify aggregation rates for various particles with different surface functionalizations. We will present single-dimer and ensemble aggregation rates of particles coated with and without biofunctionalization (IgG, streptavidin) and antifouling coatings, showing aggregation rate differences of orders of magnitude. Experiments in buffer solutions and blood plasma are described, together with a theoretical framework to unravel the role of heterogeneity in particle aggregation processes.

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OC048

Characterization of heparin-mediated aggregation of native neuropeptide somatostatin-14: importance of protofilament interactions in amyloid formation

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Glycosaminoglycans (GAGs), such as heparin, have been reported to play a significant role in amyloid formation of a wide range of proteins/peptides either associated with diseases or native biological functions. However, the specific mechanism by which GAGs promote amyloid formation and effects of GAGs on amyloid nanostructure are not fully understood. By combining microscopic, scattering and spectroscopic techniques we studied the influence of the GAG, heparin on the self-assembling kinetics, molecular structure, nanostructure morphology, and macroscopic phases of neuropeptide somatostatin-14¹. We show that two different types of assemblies are formed in the presence and absence of heparin, particulate precipitates, and liquid crystalline gels respectively. Despite the fact that both types of assemblies are reversible, heparin-peptide assembly showed slower release rate. Even though nanofibrils were observed for both types of assemblies, presence of heparin promotes the formation of unstructured aggregates. Thioflavin T results suggest that electrostatic interactions between positively charged peptide and negatively charged sulphate groups of heparin are the driving and limiting factor in the self-assembly process. According to infrared spectroscopic data, heparin hinders the formation of parallel β -sheet networks between protofilaments. Furthermore, SAXS data reveal that in the early stage of aggregation process, heparin promotes oligomer formation. Based on our results, we propose that, in the presence of heparin, the peptide rapidly precipitates into protofilaments intercalated by heparin which leads to relatively large and disordered precipitates in solution. Our findings provide insights into the nature of peptide-GAGs interactions and also highlight the danger of using GAGs in amyloid studies, particularly when concluding on structure-function relationships.

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Self-assembly of nanorods in polymer solution

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Colloidal nanorods made of semiconductors or noble metals, exhibit useful and tuneable properties that depend on their size, and also on how they are ordered on larger scales.¹ How they assemble is highly dependent on the interactions between the rods, and also the local environment. One way to cause nanorods to assemble into an ordered structure is the addition of a polymer depletant.² Adding this depletant applies an osmotic pressure to the nanorods causing them to assemble into liquid-like droplet or an ordered phase (nematic, smectic or crystal), depending on the relative polymer size and concentration of the two components. We examined the phase behaviour of this system using CdSe nanorods with polystyrene of different molecular weights as a depletant. Using SAXS we determined the phases formed under different polymer concentrations. To gain further insight into the system, we performed Monte-Carlo simulations, modelling the nanorods as spherocylinders and the polystyrene as interpenetrating spheres with radius equal to the radius of gyration. Using these two techniques we found a relationship between the phases formed and whether they formed monolayers of rods, or multilayers. We saw a close relationship between the concentration of polymer and which phases were stable depending on the number of layers, polymer concentration and polymer size.

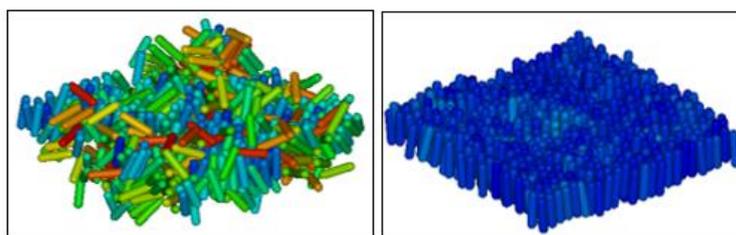


Figure 1. Favoured monolayer structures at 6kg/mol polymer volume fractions of 0.5 (left, Isotropic) and 0.55 (right, Crystal)

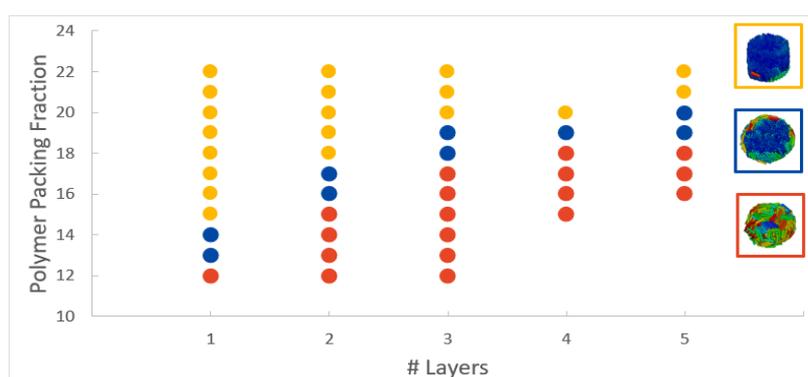


Figure 2. The phases formed in simulation with 60Kg/mol polymer as a function of number of layers and polymer fraction. Red Circle: Isotropic; Blue Triangle: Smectic; Yellow Diamond: Crystal.

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OC050

Modelling hard-rod suspensions for use in molecular-dynamics simulations

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We propose a coarse-grained model for molecular-dynamics simulations of hard-rod suspensions (either pure rod liquids or rod-polymer mixtures). Individual rods are represented by a chain of overlapping identical hard spheres, which interact through a pseudo-hard-core potential based on the cut-and-shifted Mie (generalized Lennard-Jones) potential. For the rod-polymer mixtures, the polymers are modeled as freely inter-penetrable spheres with respect to each other, while there is the pseudo-hard-core repulsion between the rod spheres and polymers. The solvent in the suspension is considered implicitly by applying a dissipative particle dynamics (DPD) thermostat: each sphere has a DPD "coat", which interacts with others via pairwise, momentum-conserving frictional and dissipative forces. We perform continuous compression and expansion simulations to study the phase behaviour of hard-rod suspensions. The estimated phase boundaries are compared with previous predictions based on the theoretical calculations and Monte Carlo simulations. The model shows the expected phase behaviours and boundaries for hard-rod suspensions, and is suited to study the self-assembly and nucleation in such suspensions.

OC051

Exploring asymmetry in nanoparticle superstructures

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Successful design and implementation of nanocrystal assemblies into functional superstructures requires knowledge of the positional tolerances required for specific optical responses. This encompasses challenges across the assembly of nanocrystals, and the measurement of their optical properties. Spatial confinement of conduction electrons in metal nanocrystals leads to localised surface plasmon resonances (LSPR) and concomitant enhancement of the electromagnetic field close to the nanoparticle surface (near field). The near-fields of two nanoparticles located close to one another interact to create localised areas of extremely high field enhancement. The coupling between adjacent nanocrystals is dependent upon the distance between the particles, the individual nanocrystal shape and the overall geometry of the superstructure. Asymmetry within a superstructure may be derived from either the intrinsic nanocrystal geometry itself. Alternatively, there may be asymmetry in the arrangement of the nanocrystals with respect to one another. Assembly schemes capable of achieving high yields of a target nanostructure, and with the flexibility to assemble different sizes, shapes and materials will be described. Progressive changes in optical properties as the symmetry of the nanocrystal building-block is reduced from highly symmetric zero-dimensional spheres through to triangular nanoprisms will be described. Asymmetry in the arrangement of the nanocrystals may take the form of large geometrical variations which, whilst remaining largely symmetrical, exhibit markedly different coupled plasmon resonance modes. These show differences both in the energy of the resultant resonance/s and the spatial distribution of the near-field over the superstructure. Small offsets from this symmetry can result in the appearance of coupled modes undetected previously. This will be discussed along with the polarization-independence of highly symmetric assemblies. Geometrical requirements to achieve a specifically designed coupled localised surface plasmon resonance signature from a nanocrystal assembly are strict and highly important. This has implications for the future design and realisation of functional nanocrystal superstructures.

OC052

Femtoliter surface droplets with dual functionalities for nanoextraction and online microanalysis

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We present a versatile, fast and effective surface droplet-based approach for liquid-liquid extraction and online microanalysis. The strategy takes advantage of the excellent long-term stability of femtoliter surface droplets for functionalization by interfacial silver nanoparticles produced by droplet reactions. Large surface-to-volume ratio of nanoparticle-armored femtoliter droplets contributes to fast extraction of hydrophobic compounds from the solution, due to the high partition coefficient in the droplets. Quantification of the extracted analytes is achieved by in-situ Raman spectroscopy with enhancement from the nanoparticles on the droplet surface. The proposed approach shows a detection limit of 0.5 nM for a model chemical of Rhodamine 6G and an excellent linear region of the signal intensity as the compound concentration spans over 3 magnitudes from 1 nM to 1 μ M. All the steps from formation and functionalization of femtoliter droplets to nanoextraction and online analysis are integrated in a simple and time-effective fluid system. The system is featured with excellent consistency, high sensitivity and extremely low detection limit. This work significantly expands the spectrum of liquid-liquid microextraction as a key sample pre-treatment technique in chemical analysis.

OC053

Femtoliter droplets on a microlens: formation and application

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Evolution of small-volume liquid on a curved surface is critical to many interfacial processes, such as water collection, vapor condensation in cooling devices and drop self-removal on anti-icing surfaces. In this work, we experimentally and theoretically investigate the morphological transition of femtoliter liquid on the surface of a 10 μm lens surrounded by a planar area. The formation of the droplet started from the rim of the microlens with the surrounding planar area less wettable for the droplet liquid. Such different wettability has led to a unique structure with the droplet partially covered the microlens. As the droplet liquid volume increased, the droplet upfront expanded along the microlens surface with the boundary maximally overlapped with the rim of the microlens. The morphology exhibited by the liquid was in good agreement with the prediction from our simulations based on the interfacial energy minimization with the pinned boundary condition. The findings in this work may be valuable for understanding and controlling of a tiny amount of liquid or the early stage growth of droplets on microstructured substrates. The obtained structures of droplet partially covered microlens have provided new opportunities to simply produce unconventional flexible polymer microlens arrays with low cost. We demonstrate that the obtained transparent polymer microlens arrays can improve light efficiency to 20% in the optoelectronic device.

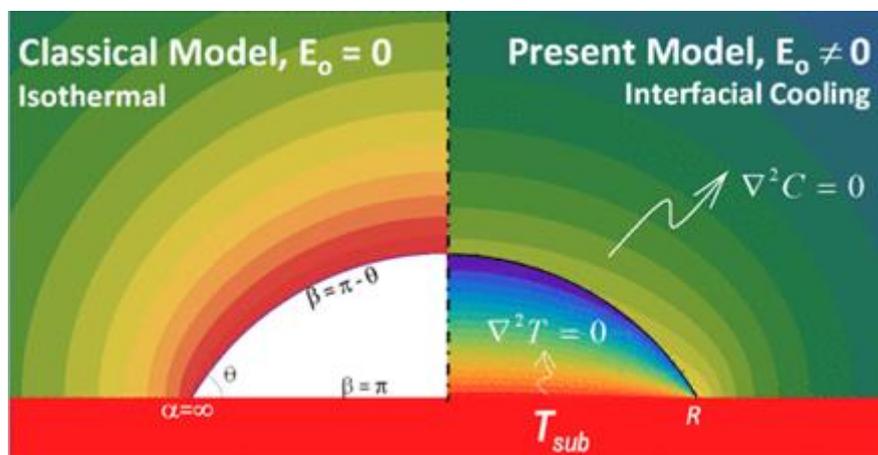
OC054

A fully coupled analytical model of sessile droplet evaporation with combined effects of substrate conductivity and interfacial cooling

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Current analytical models for sessile droplet evaporation do not consider the nonuniform temperature fields within the droplet and the underlying substrate and can overpredict the evaporation by 20%. This deviation can be attributed to a significant temperature drop due to the release of the latent heat of evaporation along the air–liquid interface. We report, for the first time, a fully coupled analytical solution of sessile droplet evaporation with the combined effects of this interfacial cooling and the substrate thermal conductivity. The two-way coupling model of the quasi-steady thermal diffusions within the droplet and the underlying substrate, and the quasi-steady diffusion-controlled droplet evaporation is conveniently solved in the toroidal coordinate system by applying the method of separation of variables. Our new analytical model for the coupled vapor concentration and temperature fields is in the closed form and is applicable for a full range of spherical-cap shape droplets of different contact angles, types of fluids, and thermal properties of the underlying substrate. Our analytical results are uniquely quantified by a dimensionless evaporative cooling number E_0 , whose magnitude is determined only by the thermophysical properties of the liquid and the atmosphere. Accordingly, the larger the magnitude of E_0 , the more significant the effect of the evaporative cooling, which results in stronger suppression on the evaporation rate. The classical isothermal model is recovered if the temperature gradient along the air–liquid interface is negligible ($E_0 = 0$) and the substrate is isothermal (very high thermal conductivities). Our findings pose interesting challenges but also guidance for experimental investigations.



OC055

Composition of surfaces of salty solutions

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The presentation focuses on the role of aerosol particles formed over the ocean in altering global climate and coastal pollution. The interfacial composition of sea spray aerosols are investigated which control key chemical reactions in the atmosphere. Knowledge of this surface composition is critical for understanding how sea spray aerosols grow and form clouds, and how they control ozone emissions and the lifetime of methane in the atmosphere. Because liquid interfaces are only a few molecules thick, we analyze the composition of sea spray droplets as function of the depth with high depth resolution. The method used for measuring the concentration depth profiles is neutral impact collision ion scattering spectroscopy (NICISS).

The surfaces investigated are firstly solutions with pure salts as solute and secondly liquid surfaces enriched with organic substances. The solvents investigated are glycerol and water. In the first case the focus is on salty solution with salts varying the anion. Solution of the sodium halides in glycerol and water are investigated. In the second case sodium halides added to surfaces of glycerol and water are investigated which are covered with mono-glycerides. The position of the halide ions relative to the outermost layer is depending on the halide anion and whether or not the surface is covered with mono-glycerides.

OC056

Small molecule profiles between lipid bilayers by neutron diffraction

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While well established for studying the internal structure of bilayers and orientation of peptides and proteins with respect to bilayers, neutron lamellar diffraction has a powerful insight the average locus of solubilisation of small molecules in stacks of lipid bilayers¹⁻³. The approach has provided unique insights into important issues in anhydrobiology and cryobiology, where previously only molecular dynamics simulations (MD) had been able to provide molecular scale insights. Currently we use the methodology to understand the interaction of cryoprotectants with bilayers, with the aim of providing important validation of MD parameters to further enhance the utility of the method. Here we discuss the experimental approach, both in terms of the use of contrast variation and the use of selective deuteration to simplify the extraction of scattering length density profiles within the bilayer.

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OC057

Effect of embedment of functional siRNA on cubic phase

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“Pegylated” Lipid-siRNA Cuboplex

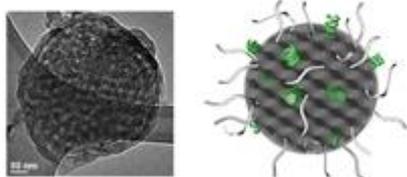


Fig 1 Schematic representation of the spherical PEGylated cuboplex particles with internal Im3m cubic structure

The cell membrane environment, which is ubiquitous in biological systems, provides an exceptional model to devise “smart nanostructures” based on the molecular self-assembly of biological macromolecules such as carbohydrates, lipids, nucleic acids, and proteins. Amphiphilic biomolecules such as lipids can self-assemble into nanostructures of well-defined geometry. ¹ Lipid-DNA self-assembly and their application in gene delivery through lipid cell membrane is a significant field of research in biological science. Cationic surfactants can make the DNA in more condensed form, which could increase the crossing rate through the membrane with highly protective environment². To date the assembly of DNA double helix and cationic or zwitterionic surfactants has been studied and which can form different to lyotropic liquid crystalline structures including lamellar, normal and reverse hexagonal and cubic phase.³ The lipidic cubic phase offers a range of advantages compared to liposomes, which have been more commonly used for gene delivery. The intrinsic properties of the bicontinuous cubic phases make it a highly efficient lipid vector for endosomal escape and cellular delivery of siRNA. For example, the modified cuboplexes may improve cellular uptake due to a high curvature which can enhance the fusion with the cell membrane. Previous research by Leal *et al.* has demonstrated the potential of PEGylated cuboplexes (Fig.1) to “deliver siRNA and specifically knockdown genes that surpass those achieved by traditional lipoplex systems. ⁴ Our main focus is on cationic-cuboplexes, complex mixture of different lipidic materials which provided us different size of lipidic cubic phase. On the basis of the size of cubic lattice parameter, it allowed us to load the functional siRNA. We also investigated the structure-property relationships between the lipid nanostructure and the encapsulated siRNA molecules by using the HTS formulation and characterization techniques.

OC058

Interface modification using self-assembly of polymer brushes and colloids in solar cells

Mukundan Thelakkat¹

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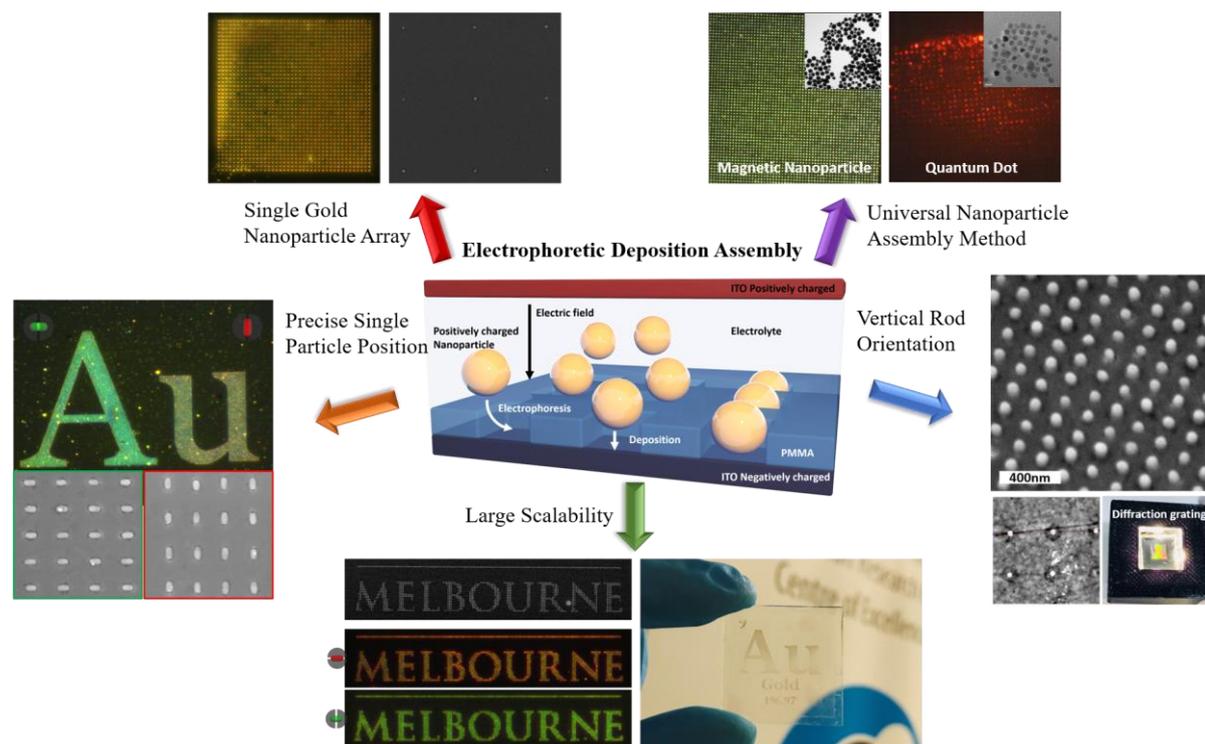
The field of thin film solar cells suffers from optical losses and charge extraction losses. In order to improve the device efficiency, both photon management and efficient charge extraction require special attention. In this talk, both these points are addressed using different approaches. In the first approach, we investigated the potential of plasmonic gold monolayers at different interfaces of P3HT:PCBM based inverted organic solar cell in order to study the trade-offs between parasitic absorption and plasmonic enhancement. We show that the plasmonic monolayer near to the top electrode spatially redistributed the light and charge generation close to the electrode leading to an improved device performance. To realize charge extraction, highly efficient charge transporting p- or n-type layers are essential to boost the performance of p-i-n thin layer solar cells. In a self-assembly approach, we demonstrate how ultrathin (3-4 nm) poly(3-hexylthiophene) P3HT layers with high charge carrier mobility can be grafted onto any polar substrate. To evaluate the charge carrier transport, P3HT chains with alkyne end groups were synthesized and chemically coupled to a surface immobilized self-assembled monolayer (SAM) having azide functionality in an OFET channel. The monolayers are in the true brush regime and the aggregation behavior of the films is characterized by UV-Vis spectroscopy and compared to linear P3HT and a bottlebrush copolymer PS-*g*-P3HT with similar P3HT lengths. For such a SAM-based organic field-effect transistor (SAMFET) nanodevice with an ultrathin P3HT layer of 3-4 nm, a very high field effect mobility of up to $1.8 \cdot 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ is achieved in channel lengths of 5 to 20 μm , which is nearly two orders of magnitude higher than reported values for polymer based SAMFETs. Both concepts demonstrate that with the help of interface modifications using suitable self-assembly or colloidal assembly techniques, important issues in devices can be successfully addressed.

Direct assembly of single nanoparticle arrays

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Nanocrystals are of great scientific interest as they exhibit unique, size-dependent optical, magnetic and electronic properties. However, a fundamental challenge that inhibits their application is assembly. Hence there is a need to position single nanocrystals with nanometre precision on a substrate for integration into solid-state devices. In this work, an efficient approach to single nanoparticle assembly – Electrophoretic Deposition (EPD) - will be discussed¹. The successful assembly of gold nanoparticle arrays by EPD will be demonstrated. Numerous parameters, such as applied potential, electrolyte concentration, and cell current, control the EPD process. Both gold nanospheres and gold nanorods have been successfully assembled into an array via EPD. The Au NRs can be deposited into the pattern with precise orientation. Furthermore, vertical gold nanorod arrays can also be achieved through EPD assembly, which is believed to be one of the most efficient methods for assembly of vertically aligned nanorods. To demonstrate the universality of the EPD assembly method, preparation of arrays of both fluorescent and magnetic nanoparticles will also be presented. We conclude that electrophoretic deposition assembly is a universal fabrication method for single nanoparticle patterning and assembly and represents a robust platform for nanotechnology-based device construction.



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Self-assembled nanocrystals as advanced optoelectronic materials

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The self-assembly of nano-materials is fundamental for achieving powerful applications in macroscopic systems. However, it remains still challenging to fully control the assembly of nanocrystals into discrete groupings. Thanks to the base-pair recognition and high binding specificity to nanocrystals, thiolated DNA has become a key ligand in the controlled assembly of nano-objects. The prime challenge when constructing discrete assemblies is to control the number of binding ligands per particle. If it is too high, particles self-assemble into 3D networks. This work will describe the principles to achieve well-defined and stable assemblies of both metallic and semiconductor nanocrystals for better understanding of optoelectronic properties. These are fabricated by controlling the DNA density on individual nanostructures. To do so, we use electrophoresis to separate particles with a controlled number of DNA strands.¹ Mixing particles with complementary DNA strands and of controlled ligand density results in the specific formation of complex nanostructures. This approach was used for gold nanoparticles to produce and purify high yield of dimers, trimers and tetramers, with the later showing three-dimensional arrangement of the nanocrystals. This approach is then translated to form discrete assemblies of semiconductor nanocrystals by functionalizing the quantum dots with thiolated DNA. The successful attachment of DNA with both core and core-shell QDs (Figure 1a and 1b) will be outlined. The binding ratio of QD to DNA is comparable with the already developed gold-DNA system. The research outlined forms the basis for the assembly of further discrete QD super-assemblies, with control over interparticle separation and three-dimensional placement of the nanocrystals. These have potential for applications in nano-optics, as well as solar photovoltaics.

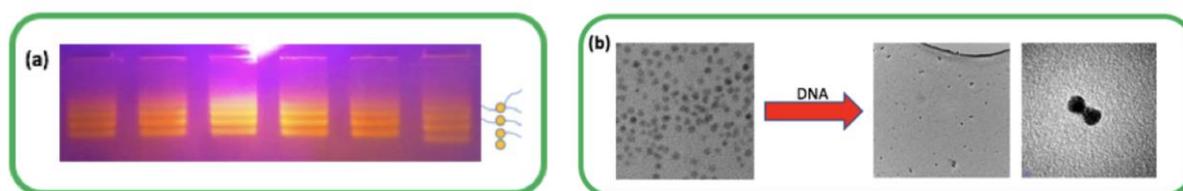


Figure 1. (a) Agarose gel electrophoresis of CdSe(CdS)₄ quantum dots. (b) TEM images of the QDs dimers held together by the thiolated DNA

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OC061

Symmetry splitting of impacting droplets on partly wetting surfaces

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The interface impact of liquid droplets on hard surfaces is of importance in many industrial and natural processes. Although water repellence induced by surface patterning is understood in static systems, its influence in dynamic systems is less obvious. Of interest in this study is the quantitative understanding of droplet shape dependence on surface patterning, which has previously been approached qualitatively.¹ This presentation advances on previous work² with the aim to explain the emergence of fingers in the outer spreading rim in relation to the impact region shape (Fig 1). Impact region shape and size is described as a function of the impact energetics and the microstructure design. Of interest in this study is the early stage wettability of microstructured surfaces. Energetics of the three-phase contact line movement through the microstructure is presented as a method for explaining droplet outcomes.

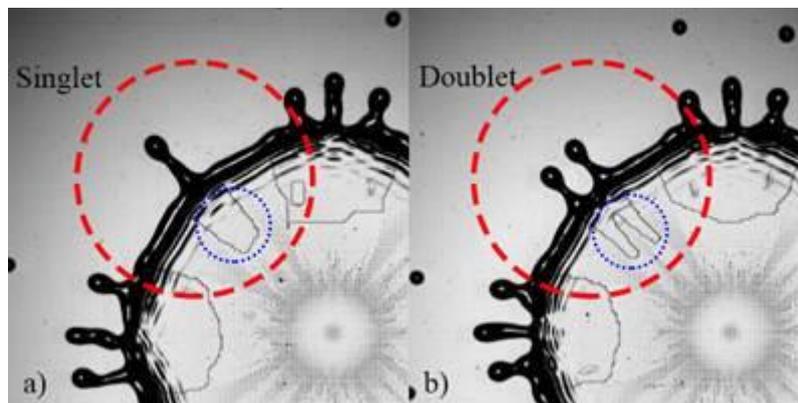


Fig 1: Droplet outcomes on microstructured surfaces consisting of 20 μm square pillars with 60 μm pitch and 15.8 μm height, producing a) a singlet off axis finger, b) a doublet off axis finger.

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OC062

Drop chains: A microfluidic approach to understanding attraction between drops in polymer surfactant systems

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Attractive interactions between drops in which aggregation, rather than coalescence occurs, lead to the formation of aggregates, gels or microstructures that then control the phase behaviour, stability, rheology and most importantly function of formulated products (*e.g.*, food, personal care products, pharmaceutical formulations). These forces are often highly system specific and are a function of a number of additive components. This talk will focus on a new method using a microfluidic device to measure the attractive surface forces between drops that arise from multi-component complex fluids including polymers, polyelectrolytes or polymer-surfactant systems. Through previous work comparing the interactions between SDS and PVP in the microfluidic system and atomic force microscopy (AFM) measurements, the effects of adsorption kinetics and drop size were identified as influential parameters. This presentation will extend these findings by exploring these aspects in further detail.

OC063

From rings to bumps in colloid patterning: the effect of short chain amphiphiles

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Spotting and evaporation of drops of nanoparticle dispersions is a key strategy for fabricating functional materials from nanoparticles (1-5). The evaporating droplet is used as a vehicle for organising the nanoparticles suspended within it into two and three-dimensional structures. The challenge is to control the liquid flow and hence manipulate the direction of the particle flux. Adding surfactant molecules, such as quaternary ammonium salts, alters the flow patterns in a predictable way by generating surface tension gradients. This approach, however, is complicated by surfactant adsorption onto the particle surfaces. It alters the interactions between the particles which can also influence the direction of the particle flux. We have investigated the effect of adding primary amines with shorter chain lengths. These amines are highly soluble in water and have high critical micelle concentrations. The particle surfaces were systematically modified by controlling the amine concentration and chain length. We found that adsorption of the amines alter the interactions between the particles and substrate sufficiently to cause the deposit morphology to change from being shaped like a ring to a uniform, circular shape. We showed that the extent of the change in deposit morphology is linked to the magnitude of the change in particle charge and the substrate wettability and hence to the length of the amine hydrocarbon chain.

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OC064

The effect of humidity and temperature on a dry, thermoresponsive polymer brush

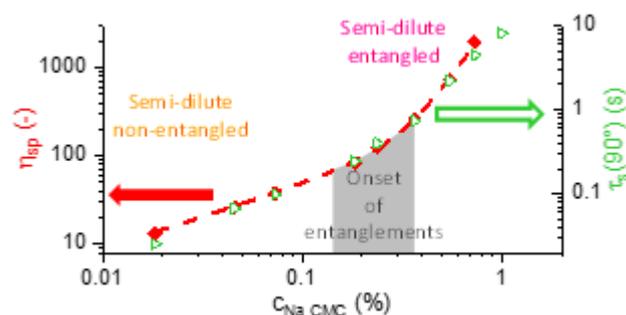
Isaac Gresham¹, Ben Humphreys², Edwin Johnson², Patrick Spicer¹, Stuart Prescott¹, Andrew Nelson³

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Surfaces decorated with densely-tethered polymer chains – referred to as polymer brushes – have been shown to possess desirable properties that are dependent on the structure of the polymer layer. Furthermore, these surfaces can be engineered to exhibit a structural response to stimuli such as pH, temperature, and the presence of specific ions and molecules, resulting in surfaces with controllable properties. One well-studied system is the Poly(*N*-isopropylacrylamide) (PNIPAM) brush which, when solvated, exhibits a lower-critical solution temperature type behaviour, transitioning from a swollen to collapsed state as temperature is increased. Whilst the stimuli response of solvated PNIPAM brushes are well characterised, little is known of the response exhibited by unsolvated ‘dry’ polymer brushes, which are primarily of interest due to their potential as sensing surfaces. These layers have previously been shown to respond to changes in solvent partial pressure, but other avenues of response have not been investigated. Here we start to address this deficiency, presenting a neutron reflectometry study on the effects of both water partial pressure and temperature on the water content and thickness of a PNIPAM polymer brush. Using our powerful reflectometry analysis platform we are able to observe significant changes in solvent content with both temperature and humidity; these changes are compared to existing brush theory. Dynamics of the dry brush response are also characterised, including the formation of voids within the brush upon a sudden reduction in water partial pressure. These findings have implications for the characterisation of dry polymer brush systems, as well as for the development of polymer brush based sensing surfaces.

Structure-property relationships of sodium carboxymethyl cellulose (Na-CMC) characterised with rheology and light scatteringJuliette Behra¹, Johan Mattsson², Olivier Cayre¹, Timothy Hunter¹¹*School of Chemical and Process Engineering, University of Leeds, Leeds, United Kingdom* ²*School of Physics, University of Leeds, Leeds, United Kingdom*

Sodium carboxymethyl cellulose (Na-CMC) is a water-soluble negatively charged linear polyelectrolyte derived from cellulose, widely used in the food and personal care industries to provide structure control to formulated products. For example, it helps in maintaining bread moisture, as well as controlling the viscosity of beverages and aids in stabilising emulsions. Its behaviour in water is known to be complex and a function of several parameters including the characteristics of the polymer (e.g. molecular weight, substitution) as well as the solution concentration and dissolution conditions. The purpose of this study was to investigate the behaviour of aqueous Na-CMC solutions over a wide range of concentrations using rheology and light scattering (LS). The concentration dependence of the low-shear viscosity region was determined with three concentration regimes being identified, where the usual scaling models would predict four. Here, the concentrated regime is absent and the entanglement concentration was found to be higher than predicted by the scaling theory. LS measurements were performed over a broad range of concentrations starting from the semi-dilute non-entangled regime. Three relaxation modes were observed, with the third mode having a much longer relaxation time (ca. 10-300 s) and significantly complicating LS measurements, which could not be removed neither by centrifugation nor filtration. It was possible to circumvent this complication by developing a new method to collect and analyse the LS data. The first two modes, diffusive, were attributed to the fast and slow relaxation modes typically observed in salt-free or not-fully screened polyelectrolyte solutions. The concentration-dependence of the slow mode diffusion coefficient D_s showed a crossover concentration, which could be compared directly to the entanglement concentration found with rheology measurements and allowed us to propose a model for the structure of the solutions.



OC066

SPATZ: The second time-of-flight neutron reflectometer at the OPAL research reactor

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¹ACNS, ANSTO, Lucas Heights, Australia

Neutron reflectometry is a powerful technique for studying the structure of surfaces and interfaces at the nanometer. The useful properties of neutrons allows for isotopic contrast variation in multi-component systems and being able to investigate phenomena under a wide variety of sample environments. At the OPAL Research Reactor there is currently one operating neutron reflectometer – PLATYPUS, however demand is sufficient that a second is needed. In September 2015, an agreement was signed between HZB and ANSTO to transfer the V18 ‘BioRef’ time-of-flight neutron reflectometer [1], previously situated at the 10 MW BER-II Research Reactor, to the OPAL Research Reactor. During 2016, a joint team of ANSTO and HZB personnel carefully disassembled BioRef and packed it into shipping containers for transport to ANSTO. BioRef arrived at ANSTO in early 2017 and is known as SPATZ (German for Sparrow) and will be the 15th neutron-scattering instrument at OPAL.

SPATZ has a vertical sample geometry, which complements PLATYPUS with its horizontal sample geometry. The vertical sample geometry will allow for use of sample environments which cannot be currently used on PLATYPUS due to geometry constraints and allows for wide-angle diffraction from multilayers and lamellar stacks. SPATZ will also be equipped for simultaneous infra-red spectroscopy and reflectometry experiments.

The instrument views the OPAL cold neutron source (CNS) by taking the end position of the CG2B guide, which has recently been installed.

SPATZ is scheduled to start hot commissioning in October/November 2018 and start user experiments in early 2019. This presentation will provide an overview of the project, its current status, and future direction. Feedback from the colloid and interface community is encouraged.

[1] M. Strobl et al., *Rev. Sci. Instrum.* **82**, 055101 (2011)

OC068

Soft, but strong, bacterial cellulose microcapsules

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Microcapsules are of interest as vehicles for encapsulating a diverse range of commercially valuable materials, including pharmaceutical, flavors, and cells. Key microcapsule attributes are the mechanical properties, providing a robust protective barrier for the contents, as well as porosity that is used to control interaction with the environment via slow release or reaction. Most approaches, including interfacial self-assembly and template polymerisation, produce strong but rigid microcapsules. Soft, elastic microcapsules can also enhance distribution and circulation time, for example for improved cell surface binding. Here, we develop a process to produce uniquely strong, but soft, porous capsules using a bio-interfacial process. We envision using the capsules to protect fragile cellular cargo without harming the transport of essential nutrients from the bulk environment. Bacterial cellulose is strong, flexible, and biodegradable and can be readily produced by simple bacterial cultures. The bacteria produce nanoscale fibers that connect to form highly porous microstructures at very low concentrations. In this work, we disperse bacteria in monodisperse water droplets into a gelled oil phase that prevents coalescence of the droplets but still permits bacterial respiration. The emulsion droplet interface then acts as a passive template for bacterial growth and production of cross-linked cellulose networks in the form of a core-shell structure. Growth can then be controlled to tune the shell thickness, pore size, and strength, which we then characterize using 3D confocal microscopy. The resulting cellulose microcapsules are very soft and flexible, allowing recovery of their spherical shape after compression by as much as 60% by external forces. The elasticity of the cellulose microcapsules is only 20-50 Pa, much softer than typical microcapsules, but the capsules are still quite strong and protective against abrasion or shear stresses.

OC069

Bio-selective bacteriostatic and fungistatic surfaces made of recombinant spider silk proteins

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Pathogenic microbial contaminations on the surface of e.g. medical products and the associated risk of infection are a severe problem especially in the public health care sector. Microbial colonization and subsequent biofilm formation are highly problematic, as biofilms are much more difficult to eradicate than isolated microbes. Furthermore, antimicrobial resistant strains are increasing at an alarming rate due to the overuse of antimicrobial agents. Since one critical step in biofilm formation is the initial adherence of pathogenic microbes onto a material's surface, inhibiting microbial attachment is a reasonable approach to develop material surfaces resistant to biofilm formation. There are two main strategies for inhibiting surface attachment, referred to as either active or passive resistance. While passively resistant surfaces utilize super hydrophilic or hydrophobic polymers, zwitterionic and other synthetic polymers, actively resistant ones include contact killing materials such as cationic polymers, amphiphilic polymers, antimicrobial peptides and polymeric/ composite materials loaded with antimicrobial agents. In this work, a novel passive approach was developed originating from the basic observation that some silk materials display high resistance against microbial degradation. We systematically investigated the bacteriostatic and fungistatic properties of a biotechnologically designed recombinant spider silk protein system. The adhesion behavior of various pathogens was analyzed on 2D-films (smooth and structured) and 3D-hydrogels by observing biofilm formation and by atomic force measurements of single bacteria's adhesive forces on spider silk films in comparison to other material surfaces (*B. mori* fibroin, polycaprolactone). Furthermore, the bioselective growth of fibroblasts and simultaneous repellence of microbes was demonstrated in co-culture experiments. Our results display the extraordinary potential of recombinant spider silk proteins to inhibit microbial infestation on products in the health care sector and for various other applications e.g. in the food and textile industry.

Acknowledgments:

The DAAD is kindly acknowledged for financial support through the Bayreuth-Melbourne Colloid/Polymer Network.

OC070

Tracking the adsorption of biomolecules at the cellulose interface for bio-diagnostics

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Cellulose based diagnostics are bio-friendly devices to identify or quantify the presence of pathogens or specific biomolecules. These devices require stable and functional biomolecule immobilization at the interface which is critical to engineer low cost and efficient paper bio-diagnostics. This study aims to quantify the adsorption and desorption kinetics of biomolecules (proteins and enzymes) onto cellulose and gold coated interfaces. Atomic force microscopy measurement shows that the cellulose spin-coated interfaces are smooth and have roughness of about 1 nm. Quartz Crystal Microbalance with dissipation (QCM-D) is applied to measure the sorption, rigidity, binding kinetics and interaction mechanisms of adsorbed Bovine serum albumin (BSA) and Immunoglobulin G (IgG) biomolecules at the gold and cellulose-liquid interface. BSA molecules adsorb in a flat conformation (5 nm thickness) and show a sponge like behaviour by adsorbing and desorbing water molecules at different buffer pH. Neutron reflectivity (NR) experiments reveal cellulose film thickness of 8 nm and it's swelling (2 to 3 times) in cellulose-water interface. Further NR enables the visualization and quantification of IgG biomolecule by increase contrast through the deuteration of the cellulose interface. The gained knowledge will contribute in understanding the interaction of physio-absorbed functional biomolecules with the cellulose surface, which help in improving the performance, longevity and the efficiency of low-cost cellulosic bio-diagnostics.

OC071

Linking adsorbed film properties to aqueous lubrication in polysaccharide-protein complexes

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Aqueous lubrication is critical to effective functioning of several biological systems, ranging from lubricin between cartilage surfaces in knee joints and ocular mucin films in our eyes to the lubricating action of saliva during food oral processing. The insights generated from studies on natural lubricants and synthetic polymers alike indicate that superior lubrication in such films requires a challenging combination of strongly adsorbed polymers to promote the film's wear resistance, while still maintaining a sufficiently hydrated film to provide the ideal polymer conformation for enhanced lubrication. More recent studies investigating the mechanism behind the ultra-low friction observed in human saliva propose that synergistic interactions between proline-rich proteins (PRPs) and mucins play a key role, suggesting that physical complexes form a bi-functional layered film i.e. PRPs bind mucins to the surface while glycosylated domains of mucins act like hydrated polymer brushes. Inspired by these findings, we seek to confirm this hypothesis using a well-controlled biopolymer system. Hydrated complexes were formed through electrostatic interactions between positively-charged lysozyme molecules and anionic residues on pectic polysaccharides extracted from *Plantago ovata* seeds. Boundary friction was measured between hydrophobic PDMS surfaces using a ball-and-disk tribometer, while adsorption was assessed using a combination of the Quartz-Crystal Microbalance with Dissipation monitoring (QCM-D) technique and ellipsometry. The results reveal that complexation between polysaccharides and proteins does lead to improved adsorption on hydrophobic PDMS surfaces, which in turn decreases boundary friction in sliding contact. Comparing QCM-D measurements of the complexes against their individual components, we conclude that pectic polymers maintain the film's hydration while lysozyme improves surface adsorption, thereby providing strong evidence that physical complexes can be utilised to design bi-functional surface layers. Our findings open up a range of opportunities for application in food and oral healthcare products, particularly in the use of food-compatible ingredients to control aqueous lubrication.

OC072

Nanocellulose-polyelectrolyte composite as superabsorbent

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Superabsorbent polymers (SAP), which are widely used in food, agricultural and pharmaceutical industries, can absorb around seven hundred times their own weight in distilled water [1]. Sodium polyacrylate is the most common commercial superabsorbent, but it is not eco-friendly. In this study, nanocellulose based superabsorbent composites are developed using polyelectrolytes (polyethyleneimine and chitosan) as renewable and environmental absorbent materials.

Polyelectrolytes of different molecular weights and charge densities were mixed with TEMPO oxidised (at high COO⁻ content) Bleached Eucalyptus Kraft (BEK) pulp of different solid consistency under strong shear. The composites were characterised by Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), mercury porosimetry, helium pycnometer, rheology and water/saline absorption capacity. The dried composites act as superabsorbents in water and saline (0.9 wt% NaCl). It was also found that SAP showed better wet strength when immersed in liquid. The addition of amine groups in oxidised fibres improves the mechanical strength of the composite as the polyelectrolyte acts as crosslinking agent between nanocellulose fibres. This presentation will analyse these novel cellulose based superabsorbent composites and how they can be engineered by controlling polyelectrolyte addition, charge density and fibre concentration to govern their structure-property relationship.

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OC073

The effects of hydrostatic pressure on the spectra of nanocrystals

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Although there has been immense interest in the electronic and optical properties of nanocrystals, there has been less work on the mechanical properties of nanoscale materials, due to the inherent difficulty in applying well defined loads and stresses to these materials, and the equally vexing challenge of measuring deformations. Here we present experiments on the effects of hydrostatic loading on the absorption and fluorescence spectra of both metal nanoparticles and CdSe semiconductor nanocrystals. The goal of these experiments is to determine the bulk modulus of the materials and to understand the effects of pressure on the crystal stability.

We find that the surface plasmon resonance of small spheres red-shifts, while for rods there are both blue-shifts and red-shifts due to competing effects of pressure on the conduction electron density and on the solvent refractive index. For CdSe nanocrystals, we find a blue-shift in the PL spectra right down to around 2nm in diameter. A slight size-dependence is observed below 2nm in the magnitude of the shift. Solidification of the solvent around 11GPa causes some aggregation of the particles and changes in crystal structure for CdSe. Loading and unloading cycles show only minimal hysteresis in the spectra if the pressure remains below 11GPa. In the case of gold nanoparticles, we can spectroscopically determine the bulk modulus with a precision of 10%. The value of $K_0 = 190$ GPa is significantly higher than the value for bulk gold (167 GPa).

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Resonant energy transfer in a single nanocrystal:dye assembly

Ali Abd Ali^{1,2,3}, Subashani Maniam¹, Steven Langford¹, Toby Bell¹, Alison Funston^{1,2}

¹School of Chemistry, Monash University, Clayton, Australia ²ARC Centre of Excellence in Exciton Science, Melbourne, Australia ³Department of Chemistry, College of Science, Al-Nahrain University, Baghdad, Iraq

Quantum dots (QDs) are photostable and have large absorption cross-sections at energies higher than their band-gap. These properties give them promise as solar harvesting moieties. Hybrid systems containing QDs and dyes thus have potential to exploit these properties of the inorganic material. In these systems, the QD may be exploited as the absorbing species, with subsequent directed energy transfer to the attached dye. This resonant energy transfer has been investigated in CdSe QD based assemblies, particularly QD:Dye ensembles. However, for ensemble data, only an average rate for energy transfer is able to be accessed. For samples of this type, the rate is averaged across the polydispersity of the QDs themselves as well as the ligand distribution on the QDs, which follows a Poisson distribution. Single particle measurements have been shown to overcome ensemble averaging. Here, we employ single nanoassembly spectroscopy (where the nanoassembly consists of a quantum dot and a dye) to provide a detailed dataset of intrinsic rates for energy transfer in QD:dye systems. We demonstrate energy transfer from single CdSe QDs to covalently linked naphthalene diimide (NDI) dyes. The photoluminescence (PL) trajectories, decay profiles, and spectra were collected synchronously from single assemblies at the two different wavelengths characteristic for CdSe QD, and NDI (Figure 1). The spectral data collected concurrently with the photon trajectories allows for exact calculation of the spectral overlap between QD and NDI, without the effects of QD polydispersity, in addition to unambiguous verification of energy transfer within the single nanoassembly. A distribution of energy transfer rates was observed for a given linker length. The reasons for this will be discussed and the results for different linker lengths presented.

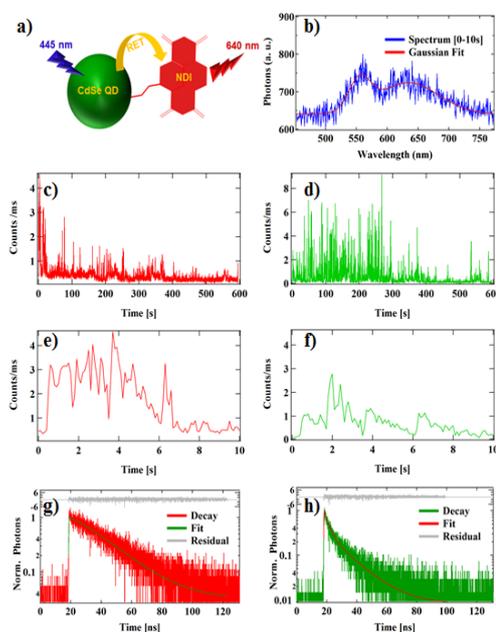


Figure 1. a) QD:NDI assembly. b) PL spectra. c), d) PL trajectories at two emissions. e), f) PL trajectories at 10s. g), h) decay profiles.

OC075

Excitonic processes in diketopyrrolopyrrole derivatives

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Diketopyrrolopyrrole (DPP) derivatives have been proposed as promising candidates for a variety of applications including the active component in photovoltaic devices and as potential singlet fission materials. Thiophene substitution lowers the bandgap of DPP derivatives allowing absorption by a broad range of the solar spectrum. Nanoparticles of DPP have been synthesised using the method of reprecipitation where the DPP in a compatible solvent is injected into a non-solvent resulting in a broad size distribution of particles, which is subsequently refined using syringe filters with various size cut-offs. These studies have shed light on the effect of particle size on the photophysical properties.

In this work we synthesised nanoparticles of a series of DPP derivatives, as well as DPP chromophores modified with a PEG chain to produce micelles of DPP, and we investigated the resulting packing of the molecules and maturation of particles using steady-state spectroscopic techniques and transmission electron microscopy. In addition, we have applied transient absorption spectroscopy and time-resolved emission measurements to the more well-defined systems of DPP chromophores to provide insights into the effect of structure on excitation energy relaxation pathways in these chromophore nanoparticle systems.

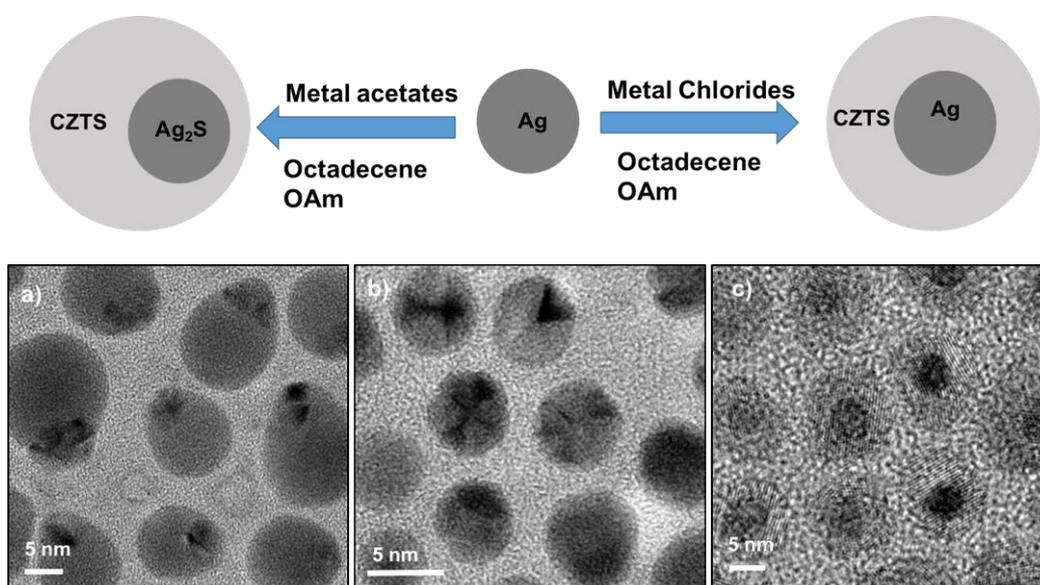
OC076

Metal-semiconductor hybrid nanostructures

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The combination of two different classes of nanomaterials, specifically semiconductor and metal, into one structure imparts the advantages of both materials in the field of electronic and optoelectronic devices. Despite this, the growth of hybrid nanoparticles containing semiconductors and metals as core-shell structures is challenging and few have been reported¹. The material copper zinc tin sulfide (CZTS) being non toxic and abundant with high absorption across the visible region and a direct band gap energy of 1.5 eV making it one of the most promising materials for harvesting solar energy. Nanocrystals composed of silver have the advantage of being able to tune the plasmon resonance into the blue, with high absorption cross-section and a higher quality plasmon resonance compared to other metals. These materials are therefore particularly appealing for the formation of functional hybrid core-shell structures as a result of their attractive optical properties and the corresponding potential for their use in devices. In this work, we report a hot injection based colloidal synthesis along with full characterization of nanoparticles composed of the plasmonic metal, silver, and CZTS. The counterions for the metal precursors, and specifically the presence of chloride ions, play an important role in the formation of a true core-shell system containing a concentric metallic Ag core. In the absence of chloride ions, the formation of Ag₂S crystals at the surface of the semiconductor nanocrystals is observed. We have also observed that the further increase in the concentration of tin(II) chloride lead to the formation of hollow CZTS structures which have potential as nanoreactors. These structures will be reported and the reasons for the different products will be discussed.



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Distance-dependent plasmon resonance coupling in nanoparticle superstructures

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Plasmonic nanoparticles of gold or silver are known for supporting localized surface plasmon resonances (LSPRs) due to their interaction with electromagnetic waves. Encapsulating these metal nanoparticles into a soft cross-linked hydrogel shell allows the possibility of forming periodic monolayers. Core-shell particles spontaneously self-assemble at an air/liquid interface fabricating hexagonally ordered superstructures. Interparticle distance can be easily varied in a large range by adjusting shell size or dwell-time. The structures can be transferred on a glass substrate. Due to the periodicity of the array LSPRs can couple to diffractive modes and thus support surface lattice resonances (SLRs). The coupling regime strongly depends on the distance between the metal cores [1]. Furthermore, SLRs can be enhanced by homogenizing the refractive index environment. To achieve this, monolayers on glass are embedded in a polymer-matrix [2]. In this contribution we show the correlation between coupling regime of SLRs and interparticle distance for hard-soft core-shell particles in hexagonally ordered monolayers. In order to investigate the plasmon coupling UV-vis extinction spectroscopy was used. Absorbance spectra nicely show differences for coupling and noncoupling regime (Fig 1). Monolayers in coupling regime show narrower resonances peaks width in contrast to noncoupling regime. Additionally, we used theoretical simulations to support the experimental data.

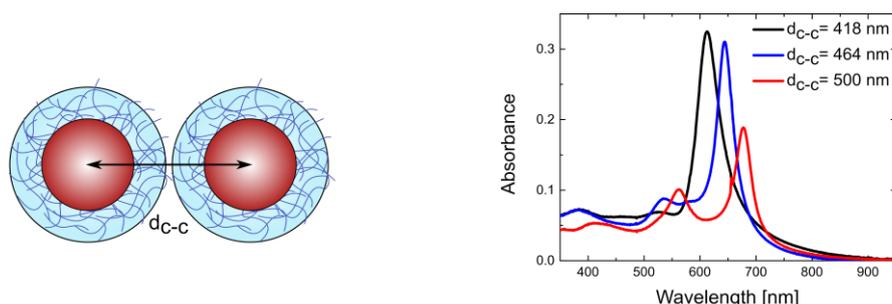


Figure 1. Left: schematic view of core-shell particles with their nearest neighbor center-to-center distance d_{c-c} . Right: Absorbance spectra of coated monolayers with varying d_{c-c} .

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OC078

Formulation of dual component solid drug nanoparticles for improved oral bioavailability of Darunavir and Ritonavir

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Many active pharmaceutical ingredients (API) exhibit poor aqueous solubility, which can often impact on the bioavailability of the drug when taken as a therapy. Recently, a strategy for formulating antiretroviral drugs into solid drug nanoparticles (SDNs) has been presented, with the resulting products exhibiting enhanced oral pharmacokinetics (PK). Preparation of these nanoparticles relies on an emulsion-templated freeze-drying method to screen different polymers and surfactants, with the drug dissolved in an organic phase and water soluble polymers and surfactants present in the aqueous phase. Once ideal excipients are identified and studied for reproducibility, stability and pharmacological behaviour, the method can be translated to spray-drying for scale-up and manufacture. Antiretroviral drugs are often taken in combinations as part of a HIV drug regimen which act on multiple viral targets. This is known as highly active antiretroviral therapy (HAART) and often involves antiretroviral drugs being administered with ritonavir, known to boost the half-life of certain antiretrovirals.

We have adopted the solid drug nanoparticle strategy with the anti-retroviral drugs Darunavir (DRV) and Ritonavir (RTV) to prepare dual component SDNs to combine two APIs into one nanoparticle-containing powder feedstock. *In vitro* pharmacological testing isolated the best performing formulation by determining the apparent permeability of the SDNs across Caco-2 and triple culture monolayers, whilst *in vivo* studies established its steady state pharmacokinetic profile. Steady-state multiple-dosing studies determined, using an initial loading dose followed by a 50 % lower maintenance dose, that there is potential for considerable dose reduction without compromising PK exposure. This data provides preclinical demonstration of the world's first DRV/RTV fixed-dose-combination formulation with a potential for dose reduction of both DRV and RTV whilst maintaining drug concentrations in the therapeutic window. The scale-up of the best SDN candidate by spray-drying has provided the manufacturing scale necessary to potentially pursue first in human clinical evaluation.

OC079

Overcoming challenges for drug delivery towards poorly endocytic cells in the fight of malaria and haematological malignancies

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Nanotechnology has revolutionized healthcare, medicine and the way we understand cellular and physical processes below the micron scale. A colossal number of new nanocarriers and targeted drug delivery systems are being developed with promising efficacies revealed in cancer and infectious diseases during preclinical trials. Nevertheless, it is surprising though, that only those strategies relying on simple pharmacodynamic processes (e.g. increase of drug circulation times, protection against biodegradability and reducing biodistribution volumes) have been clinically approved so far.¹ Immunotoxins refer a special mention as unique cytotoxic cell-targeted approach effectively proved in the clinics.^{2,3} A correct understanding and selection of the nanocarrier type, target cell biology, drug physicochemical properties and encapsulation methods is vital when designing targeted delivery systems. Further challenges must be addressed when combating afflictions affecting poorly-endocytic cells. Two examples of particular interest due to their severe consequences are presented and include: (a) immature B cell precursors, whose overproduction is responsible for Acute Lymphoblastic Leukemia, haematological malignancy being aimed during our current research at Children's Cancer Institute, and (b) erythrocytes, host cell for the malaria-causing, blood-borne infectious agent *Plasmodium falciparum* studied in previous works (Fig.1).^{4,5} Examples of strategies followed in the past and currently being explored to overcome such limitations, e.g. study of the biology underlying receptor-antibody interactions, design of combinatorial strategies against multiple cell receptors, and the exploration of alternative drug delivery pathways to the canonical endocytic route, among others, will be discussed during the talk.

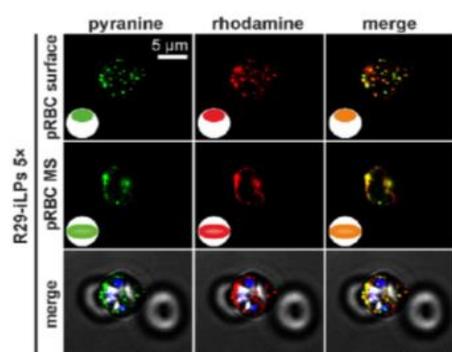


Fig.1: Targeted immunoliposomes subcellular distribution in *Plasmodium*-infected red blood cells. Pyranine/rhodamine as nanoparticle cargo/bilayer markers.⁴

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OC080

Drug delivery vehicles based on engineered spider silk proteins

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Drug delivery systems allow tissue / cell specific targeting of drugs in order to reduce total drug amounts administered to an organism and potential side effects upon systemic drug delivery. Most drug delivery systems are polymer-based, but the number of possible materials is limited since many commercially available polymers induce allergic or inflammatory responses or lack either biodegradability or the necessary stability in vivo. Spider silk proteins represent a new class of (bio)polymers that can be used as drug depots or drug delivery systems. The recombinant polyanionic spider silk protein eADF4(C16), which can be processed into different morphologies such as particles, films, or hydrogels, has been shown to fulfil most criteria necessary for its use as biomaterial. Further, eADF4(C16) particles have been shown to be well-suited as drug carriers for polycationic or neutral drugs, but cellular uptake of such particles is low. Variants of eADF4(C16) with inversed net charge or incorporated cell penetrating peptides and receptor interacting motifs show an increased cellular uptake. Further, polycationic variants allow incorporation of negatively charged drugs including high molecular weight substances, like nucleic acids.

Acknowledgments

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OC081

Using pipettes for mechanical characterization of soft colloids

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Measurement techniques such as scanning ion conductance microscopy [1,2] and aspiration [3] are based on interactions between small-scale pipettes and nearby particles or surfaces. This presentation will describe efforts to extend pipette-based sensing so that ion current measurements are used in conjunction with optical data; and to extend the use of pipettes for mechanical measurements to sub-cellular length scales. The initial work stream involved development of the experimental system [1]. This apparatus is now being used for experimentation with standard soft polymer colloids, as well as various particles of biological origin. To improve the quality of quantitative data, the measurement process is being modelled, and the most important sources of uncertainty are being identified and mitigated. One particularly important aspect of this work is accurate, non-destructive characterization of pipettes without resorting to time-consuming methods. Using simple pulling techniques, pipettes can be fabricated efficiently in comparison with micro- and nanofluidic structures. We are working to understanding the reproducibility of this process, and to develop quality control protocols for individual pipettes.

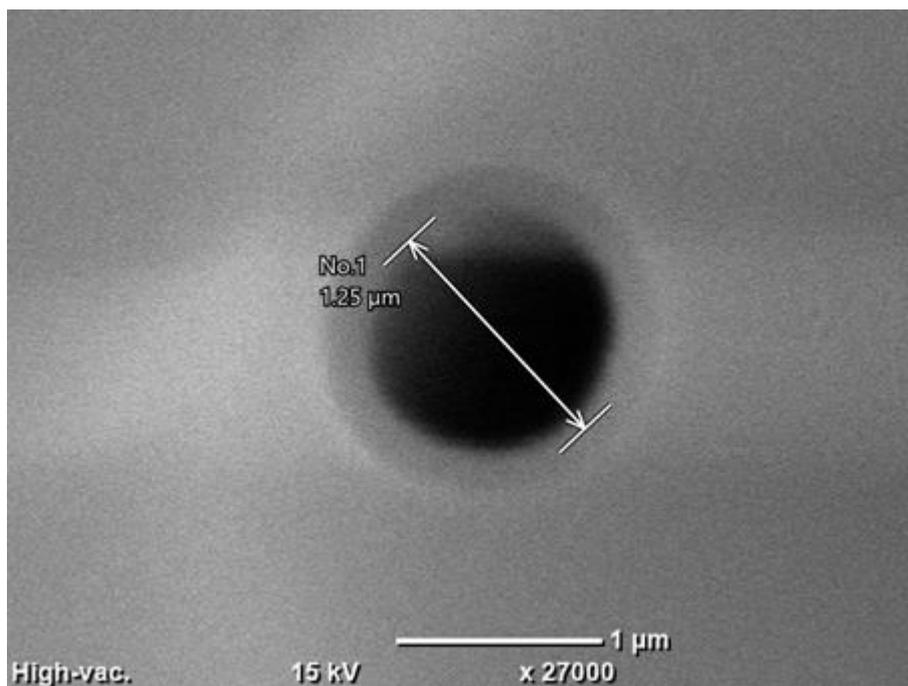


Figure: Non-destructive measurement of a silica pipette tip using desktop scanning electron microscopy.

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OC082

Rheological and acoustic properties of harvested, incubated and ruptured microalgae slurries (*Nannochloropsis* sp.) at high solids concentration

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For the minimisation of energy consumption in the production of biofuels from microalgae, there is an emphasis on processing high solids slurries. However, the increase in viscosity with the solids introduces challenges in processing the slurries through the cell rupturing equipment such as High Pressure Homogenisers (HPH) and ultrasonicators. The well-known shear thinning behaviour of microalgae suspensions adds another complication to the rheological behaviour. In this study, the rheological and acoustic properties of marine microalgae *Nannochloropsis* sp. were measured as a function of solids concentration (at 12, 20 and 24%) for a freshly harvested, incubated and ruptured pastes. All the slurries were found to be shear thinning where the shear independent viscosity was observed around a shear rate of 200 s⁻¹. The zero-shear and high-shear viscosities of the slurries increased with increase in solids concentration at all stages of processing. For a 12% solids slurry, the increase in viscosity was significant only after the cell rupture stage, whereas for a 20% solids slurry there was a significant increase in viscosity during both the stages of incubation and cell rupture. For a 24% solids slurry, there was a significant increase in viscosity with the incubation whereas there was slight increase in viscosity with the cell rupture. The zero-shear and high-shear viscosities of the slurries were predicted as a function of wet volume fraction of cells using Krieger-Dougherty model. The model explains the viscosities of freshly harvested and incubated pastes very well but not the ruptured paste. This is attributed to the fact that the ruptured paste has a lot of cell debris and ruptured cells do not have any geometrical uniformity. The shear thinning behaviour (< 1 s⁻¹) was fitted with Herschel-Bulkley model where the consistency index increased, and the flow behaviour index decreased with increase in solids concentration

OC083

Colloidal and gel assemblies of brush-like polysaccharides with motif-specific interactions

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Polysaccharide hydrocolloids are a class of biological polymers with unique physicochemical properties, versatile functionality and a broad spectrum of applications in foods, where they are used as thickening, gelling and structuring agents. Here we investigate colloidal and gel assemblies of a special class of polysaccharides found in seed mucilage of plants from the *Plantago* genus. These polysaccharides have a xylan backbone densely decorated with an array of side-chains. Almost 95% of xylose residues of the backbone are substituted, which classifies these polymers as bottle-brushes. In particular, we have isolated two gel-forming neutral bottle-brushes arabinoxylan polymers that exclusively comprise of xylose and arabinose residues. Both fractions have very similar molecular weight, monosaccharide and linkage composition, yet their rheological, structural, and thermodynamic behaviour is markedly different. Using a wide range of rheological, microscopic, and structural characterisation techniques, we have established that (i) hydrogen bonding between side chains of neighbouring molecules is a key driver of assembly; (ii) the strength of hydrogen bonding, however, is motif specific, which underpins the differences in physical properties between two fractions.

Using optical rotation dispersion and NMR we have tentatively proposed possible motif configuration of these two arabinoxylans. The polymers with a more regular motif of side chain substitutions adopt a twisted (helix-like) conformation. The regularity of the twist motif promotes hydrogen bonding between terminal xyloses, which show stronger hydrogen bonding compared to arabinoses. By contrast, the polymers with randomly distributed side chains show a markedly lower energy of hydrogen bonding and, consequently, lower gel strength and weaker water holding capacity. It is envisaged that discovery of motif-dependent interactions will open new opportunities for rational design of polysaccharides with targeted and highly tuned physical properties, providing a far-reaching potential for delivering novel tailor-made hydrocolloids for use in foods, smart materials, cosmetic, and pharmaceutical industry.

OC084

Impact of gas injection on flow and physicochemical properties of municipal sewage sludge

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Sludge flow behaviour and bubbles rise velocity in sludge is of great importance for design, optimisation and hydrodynamic operation in sludge management process. Sludge flow behaviour or in other word sludge rheology has a significant impact on bubbles size and consequently on mixing and mass transfer efficiency which are important parameters for design and scale-up. There are only few studies investigated the impact of aeration on different process parameter such as viscosity, gas holdup, etc. while the comparison between them is also difficult due to the variation of sparger type, experimental setup, and assumptions made for calculation. Moreover, there is no study to correlate changes in sludge rheological properties and gas holdup in concentrated sludge due to gas injection.

This work examines the influence of gas injection rate on physicochemical properties of sewage sludge. The impact of four different gas flow rates on 5 different concentrations of sewage sludge properties including rheological properties, soluble COD (sCOD), and suspended solids was determined. The results showed that sludge structure weakens by gas injection and elastic modulus as an indication of sludge structure strength decreases linearly with increasing gas flow rate due to shear induced by gas. We also showed that the amount of shear imposed by gas injection can be predicted using a simple model based on sludge concentration, and gas velocity. Gas injection also showed a strong impact on sludge physical properties such as zeta potential and suspended solids, soluble COD. Furthermore, the imposed shear in sewage sludge showed a logarithmic relation to the gas holdup.

This study can give us a new insight to optimise the sludge treatment process by understanding the effective viscosity and bubble behaviour in the sludge reactors.

OC085

Combining shear and compressional rheology

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Understanding suspension rheological behaviour is crucial for the design and operation of processes involving mineral slurries and wastewater treatment sludges, and for the formulation and product performance of coatings and ceramics, for example. The solid particles in concentrated suspensions form continuous particulate networks that can withstand an applied force and behave as an elastic soft solid. Suspensions flow or collapse if the force exceeds the network strength at a given volume fraction φ . The yield point in shear is often naively described by the shear yield stress $\tau_y(\varphi)$, although this has been shown to vary with the applied rate. In solid-liquid separation processes, a compressional load is applied to just the solid phase of the suspension. This is the applied pressure in filtration or the buoyant weight of the particles in sedimentation. If the load exceeds the compressive yield stress $p_y(\varphi)$, the solid phase consolidates or densifies, that is, it forms a filter cake or a sediment. Consolidation continues until the network strength is equal to the applied load.

In many solid-liquid separation processes, a shear force is applied at the same time as a compressional load, leading to improvements in separation performance since suspension strength in compression is at least an order of magnitude greater than in shear. $\tau_y(\varphi)$ is measured without wall slip using a vane in a large cup and $p_y(\varphi)$ is measured using sedimentation and filtration, but there are no suitable techniques for measuring suspension rheology under combined shear and compressional loads. We have developed several new techniques and demonstrate that, upon confinement of the particles and application of a compressive load, $\tau_y(\varphi)$ increases until it approaches $p_y(\varphi)$. This has significant implications for dewatering devices such as decanting centrifuges, belt press filters and sedimentation lagoons, as well as understanding drying and cracking phenomena.

OC086

The effect of micromixer geometry on the properties of peptide-loaded microgels

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In an effort to contribute to scalable production of polymeric carriers of antimicrobial peptides, we here investigate effects of three-dimensional (3D) printed micromixer design on microfluidic particle generation. For this purpose, micromixers of different geometric designs were used to prepare Ca²⁺-cross-linked alginate microgels, into which polymyxin B was incorporated in a continuous process. Fluid dynamic simulations were used to elucidate the flow patterns inside the micromixers, showing the three micromixer designs investigated to display flows which were either (i) turbulent with chaotic disruption, (ii) laminar with convective mixing, or (iii) convective with microvortex formation. Structural features of the microgels were characterized using dynamic light scattering, z-potential measurements, and small angle x-ray scattering. From such studies, particle size and compactness were found to depend on micromixer geometry, the smallest and most compact particles obtained when the preparation involved microvortex flows, while larger and more diffuse microgels were obtained when prepared with laminar mixing. Polymyxin B was found to localize in the particle interior, and to cause particle growth with increasing peptide loading. Ca²⁺-induced cross-linking of alginate, in turn, results in particle contraction. Peptide encapsulation efficiencies were higher than 80% for all systems investigated, but highest for the smallest particles, obtained after microvortex-mediated mixing. Ellipsometry results for surface-bound microgels demonstrated electrolyte-induced peptide release, in all cases resulting in complete peptide release at physiological ionic strength. Taken together, these findings demonstrate that microfluidic generation of microgels through 3D-printed micromixers offers promises for continuous generation of peptide-containing microgels.

OC087

In-vitro digestion profile of curcumin encapsulated in Pickering emulsions stabilized by Fe₃O₄@CNC nanocomposites

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Stimuli-responsive delivery of micro-encapsulated drug plays vital roles in enhancing the healing effects of bioactive ingredient for therapeutic treatment. In this work, using curcumin as the model drug, we report the magnetic-triggered release profile of the curcumin-loaded Pickering emulsion stabilized by Fe₃O₄@CNC (MCNC) nanocomposites *in-vitro* in simulated digestion solution and further evaluated its potential in inhibiting the growth of colon cancer cell line. The synthesized MCNC-stabilized Pickering emulsion (MCNC-PE) can effectively resist the deformation from acidic media (stomach pH). In simulated intestinal fluid (SIF), the introduction of oscillating magnetic fields increased the release of curcumin by 1.92 µg/ml.min from the microcarrier. Cell line cytotoxicity experiments were performed to evaluate the anticancer performance of curcumin-loaded MCNC-PE on colorectal cancer cell line HCT116. The preliminary results from MTT assay show that the incubation of the microcarrier with HCT116 cells inhibited the cells growth activity to 80% in 24 hours even in the absence of the external magnetic field. The implication of magnetic fields further reduces the cell viability of the HCT116 to 53% at the end of 24-hours incubation. The outcomes demonstrated the potential of the curcumin-loaded MCNC-PE as a magneto-controllable bioactive delivery carrier for colon cancer therapeutics.

OC088

A novel drug delivery vehicle for treatment of recurrent high grade glioma

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Metal microcapsules have emerged in recent years as a potential game-changer for efficient delivery of active ingredients due to their ability to fully retain a core until release is actively triggered.¹ This is particularly pertinent for drug delivery, allowing for spatial and temporal control of the release of cytotoxic drugs, potentially reducing toxic off-target side effects often associated with these compounds.

Glioblastoma multiforme (GBM) is the most aggressive primary brain tumour, and has a devastatingly poor prognosis. Current treatment involves maximal safe resection of the tumour, followed by concomitant radiotherapy and chemotherapy. However, the residual tumour left behind after surgery shows significant resistance to traditional chemotherapy, due to the inhomogeneous nature of the tumour, and the inability of the chemotherapeutic to efficiently cross the blood-brain-barrier. Localised therapies have shown promise in improving survival of GBM patients. Implantation of drug delivery devices immediately following surgical resection provides a novel solution to target the highly infiltrative tumour cells that are known to exist beyond the surgical cavity and ultimately lead to treatment failure.² Importantly, as treatment begins with surgical removal, implantable, controlled drug delivery devices can easily be integrated with standard-of-care.

Our group has made considerable progress in the development of ultrasound-responsive metal microcapsules by depositing a continuous metal shell onto polymer microcapsules or oil droplets using electroless plating, to prevent premature release. We show that when the capsules are exposed to an ultrasound field, they burst, releasing their payload. The technology and potential applications will be described in this presentation.

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OC089

Acoustically active colloids for use in ultrasound drug delivery systems

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Microbubbles are the gold standard in diagnostic ultrasound imaging. However there are several disadvantages of micron sized bubbles as uses in biomedical applications. They have short circulation times, their large size (2-10 μm) restricts them to the vasculature and they are also rapidly destroyed upon ultrasound exposure. To address these limitations, we have developed new acoustically active colloids that are capable of being ultrasound responsive. The physical properties of the acoustically active colloids have been characterised. We also demonstrate that our colloids are biocompatible and do not show cytotoxicity to cells nor haemolytic activity in blood at clinically relevant concentration. These and other results will be presented.

OC090

Acoustic enhancement of intracellular delivery for ex vivo therapeutics

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Recent advances in gene editing/therapy have highlighted the potential of *ex vivo* techniques to treat many diseases, wherein a patient's cells are harvested, engineered to insert various therapeutic agents and re-infused. Considerable challenges however remain in not just inserting these agents into cells whilst retaining their viability, but also in ensuring that they are not degraded within the cell.

Physical methods (e.g., electroporation, sonoporation, etc.), for example, allow efficient translocation through pore formation, but not without afflicting considerable damage, thus resulting in poor cellular viabilities. Biochemical methods, in contrast, rely on viral/non-viral carriers to facilitate greater endocytotic take-up. The endocytosis pathway nevertheless results in the concentration of the internalised cargo within the endosomes and lysosomes where they are degraded. Strategies that allow endosomal escape are therefore required in order for the cargo to enter the cytoplasm where they can target the nucleus more efficiently.

We show that exposure of the cells to high frequency (>10 MHz) sound waves facilitate enhances the uptake of nanoparticles, molecules and nucleic acids by several-fold, whilst retaining very high cellular viability (>97%). Unlike sonoporation, the high frequency excitation does not result in pore formation along the cell membrane but instead sufficiently disrupts the lipid structure to allow the therapeutic agent to diffuse through. This membrane permeabilisation effect is, however, transient given that the lipid structure immediately returns to its original state upon relaxation of the acoustic excitation. Such immediate recovery of the cell is the reason for the high viability observed. As this internalisation mechanism does not involve endocytosis, we observe the therapeutic cargo to be distributed throughout the cytosol instead of being localised within the endosomes/lysosomes, thus facilitating more efficient nuclear targeting and hence transfection. Indeed, with siRNA delivery into human embryonic kidney (HEK293-T) cells, we observe a two-fold knockdown in gene expression.

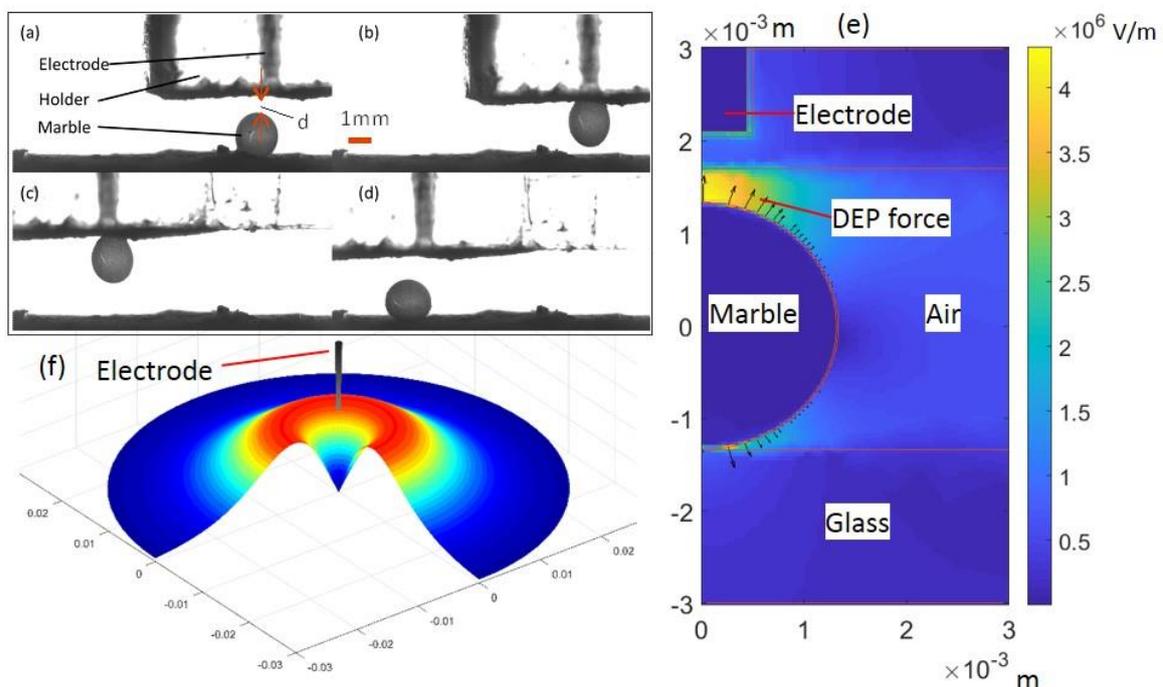
OC091

Manipulating liquid marbles using dielectrophoresis

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A liquid marble is a small droplet coated with microscopic hydrophobic powder. The non-wetting liquid marble is capable of virtually lossless liquid transport without any cross contamination. With the ability to grow cell spheroids, the liquid marble is an invaluable tool in biomedical research. We have developed and analysed the technique of manipulating liquid marbles using dielectrophoresis (DEP) in three dimensions. This technique operates based on the mismatch in permittivity between the liquid marble and its surroundings, which is automatically satisfied in most cases. Therefore, the technique can manipulate almost all liquid marbles in an open environment without material constraints. We used a simple and cost-effective setup to generate a large and non-uniform electric field. Central to this setup is a thin electrode biased to high voltage. With this setup, we demonstrated that we can repeatedly pick and place sessile liquid marbles with volumes up to 20 microliters. Furthermore, we demonstrated that liquid marbles floating on a free liquid surface can be trapped without any physical contact. Liquid marbles positioned up to 50 mm away from the electrode have been trapped. Subsequently, we could move the electrode to drive the marble to any desired location on the free surface. We demonstrated that the floating liquid marble can be driven at a speed higher than 30 mm/s. We provided a detailed theoretical model which traces the path of the marble and predicts the operational region of the marble based on experimental parameters to better understand the capability of this technique. The manipulation technique presented here can be easily applied to many existing liquid marble setups due to its non-specificity. Furthermore, our technique is highly programmable and scalable.



Liquid marbles manipulated using DEP. (a)-(d) Side view of a liquid marble being picked up by an electrode and then placed at a different location. (e) Simulation of the DEP forces that provide the lifting force. (f) A cut-out three-dimensional view of the magnitude of the self-centering DEP force field near the electrode.

OC092

Application of electrostatic particle/droplet interactions to mineral systems

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Harnessing the electrostatic interactions between a bed of particles on a charged plate and an earthed water droplet has recently been demonstrated by our group to produce liquid marbles and complex particle/liquid aggregates from colloidal polymeric particles^{1,2} and industrial mineral samples³. Here we will describe attempts to control this process, for a single 90 – 180 µm silica sample (arithmetic mean 135 µm), using the levers of aqueous solution conductivity, surface tension or viscosity. The separation distance when particles first transport to the pendent aqueous droplet is observed to be little affected by these drop properties, though the behaviour of the particles once attached is. This post-attachment behaviour greatly influences the ability of further particles to attach and be engulfed in the droplet. Further, we have investigated the applicability of the method to separating haematite and goethite mineral from their common gangue silica in the 63 – 90 µm particle size range. These three minerals separately exhibit distinctly different behaviour in the electric field, transporting to the droplet at widely different separation distances, with haematite requiring a closer separation distance to overcome the inter-particle cohesion within the bed. This difference in ease of transport is utilised in an attempt to selectively separate particles from a mixed bed.

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OC093

Effect of field characteristics on electrostatic formation of liquid marbles

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A high-voltage electric field provides an unconventional method for forming liquid marbles¹, with some distinct advantages over the traditional direct-contact method, such as the ability to incorporate hydrophilic as well as hydrophobic particles. This allows the formation of entirely new classes of liquid marble-like aggregates². Our method utilises a particle bed resting on an electrically-biased substrate, from which particles are electrostatically ejected to coat an earthed pendent droplet. The interaction of both the particles and liquid with the electric field is clearly a critical part of the process. Here, we discuss the electrical and electrostatic properties and mechanisms that determine the character of the formation process and the nature of the final aggregate. A combination of experimental data with analytical and finite-element models has been used to investigate these phenomena, which include particle and liquid conductivity, electric field morphology, packing of a charged particle bed in the field, and electrostatic deformation of the liquid drop.

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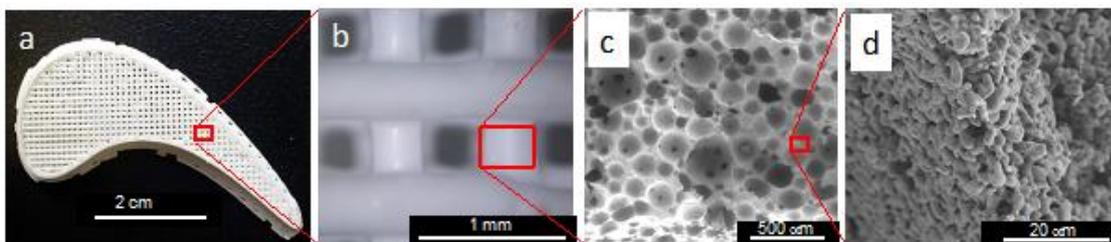
OC094

Particle stabilized foams and emulsions as pastes for 3D printing multiscale porous ceramics

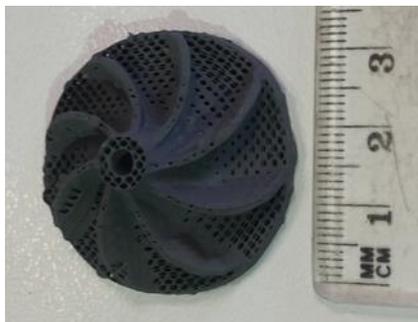
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We present an approach to producing multiscale porous ceramics using a 3D printing approach. Millimeter scale porosity is created by the 3D printed scaffold strands. We introduce 100 micron scale porosity into the scaffold strands using particle stabilized foam and emulsion paste inks. Using this approach porous ceramic strands can be 3D printed *via* the Direct Ink Writing (DIW) technique. Micron scale porosity can also be developed by partial sintering of the ceramic. The 100 micron scale porosity is created by producing particle stabilized foams or emulsions of the ceramic suspensions. The rheological (flow) properties of the foam or emulsion pastes must be carefully controlled to produce paste inks suitable for printing by extrusion through the needle of an extrusion based 3D printer. The removal of the oil phase during drying is a particularly challenging part of the process. The objects become strengthened by sintering at high temperature. Formulations have been developed for oxide and non-oxide ceramic materials. Complex shaped objects can be printed and sintered into crack free components, but distortion during drying and sintering lead to poor shape and tolerance control.



Schematic example of multiscale porous ceramic structures produced by 3D printing.



Example of sintered 3D printed ZrB₂ pump impeller shape with 72% porosity.

Sintering-free conductive inks for inkjet-printed electrochemical biosensors

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High-throughput fabrication of electrochemical sensing platforms holds remarkable promise for the production of cost-effective, versatile point-of-care diagnostic devices. Inkjet printing has emerged as a promising alternative to traditional screen-printing technology for the template-free production of well-defined, inexpensive electrodes that allows rapid prototyping. However, high-performance electrodes require suitable conductive inks composed of colloidal carbon or metallic particles. Conventionally, the ligands required for colloidal stability act as insulating barriers and must be removed in a post-deposition step. The fabrication process becomes cumbersome and incompatible with many flexible substrates and with the conjugation of biomolecules prior deposition. Recently, we have successfully demonstrated the use of conductive polymers as nanoparticle ligands to improve electron transport at particle-particle interfaces.¹ The metal content and solvent composition can be tuned to formulate inks that are suitable for inkjet printing. Here, we demonstrate the application of sintering-free metal-based nanoparticle inks to produce bio-active electrodes. Subsequently, we validate their electrochemical sensing performance for the detection of glucose. An electrically conductive polymer is bound onto gold nanoparticles (AuNPs), providing colloidal stability and excellent electrochemical performance to sintering-free inks. The polymer, poly[2-(3-thienyl)ethyloxy-4-butylsulfonate] (PTEBS), binds to the AuNPs surface and allows the physical adsorption of a bioreceptor, glucose oxidase (GOx). We confirm the strong and stable polymer binding and the subsequent GOx immobilization by means of Raman spectrometry, zeta potential measurements and X-ray photoelectron spectroscopy. Finally, we validate the performance of this bio-active ink-based electrode for the quantitative detection of glucose between 0.5 and 10 mM. Excellent reproducibility and fast response were observed. This simple fabrication of electrochemical sensor platforms opens extensive possibilities for the large-scale production of multiplexed biosensors for point-of-care diagnosis.

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Active biofilm treatment: magnetic liquid metal nanoparticles as antibacterial agents

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The rise of antibacterial resistance has made the treatment of biofilm-related diseases an on-going challenge. This situation has made the occurrence of post-operative, biofilm-based infections much more prevalent and increasingly difficult to treat. As such, the quest for next-generation antimicrobial technologies must pivot towards targeted therapies for which pathogenic species cannot develop resistance. Recently, liquid metal (LM) nanoparticles have emerged as a new class of biocompatible nanomaterial that simultaneously possess both metallic and fluidic properties. In essence, the nanoparticles are hard spheres which remain internally fluidic. Importantly, gallium-based LM particles, such as Galinstan (a Gallium-Indium-Tin alloy), can be magnetically functionalised via the incorporation of internalised magnetic iron nanoparticles. In this study, the use of magneto-responsive Galinstan based liquid metal (LM) nanoparticles is assessed as a new class of antibacterial materials. Importantly, when exposed to an oscillatory magnetic field the LM nanoparticles are physically activated, meaning that they both spin and undulate within the solution. When placed in contact with a bacterial biofilm the movement of the particles is capable of physically inactivating the bacterial cells while disrupting the surrounding dense biofilm matrix. The antibacterial efficacy of the LM nanoparticles was assessed against both Gram-positive, *Staphylococcus aureus*, and Gram-negative, *Pseudomonas aeruginosa* bacterial biofilms.

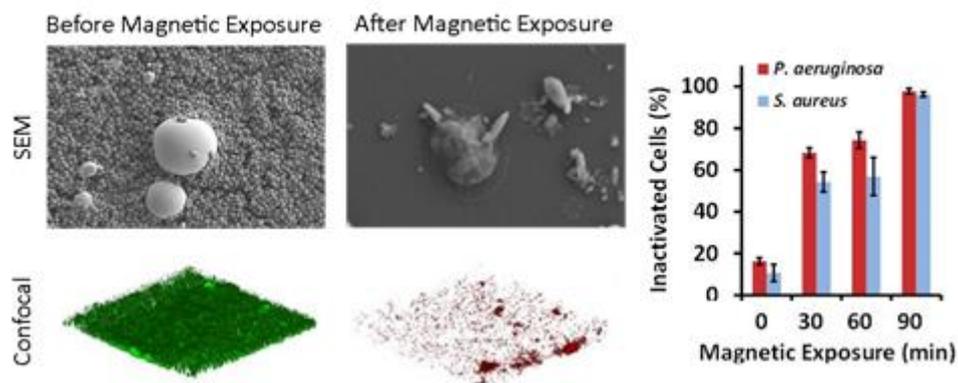


Figure 1. SEM and confocal images of a *S. aureus* biofilm in the presence of Galinstan nanoparticles before and after exposure to a magnetic field. The graph shows the relative live/dead bacterial cells as a function of exposure time (min).

OC097

Rifampicin loaded lipid nanoparticles for treating *Staphylococcus aureus* infection

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The fast increasing number of antibiotic resistant bacteria is a serious threat to our society. Nanomedicine has the potential to improve the effectiveness of currently available antibiotics. These nanomaterials can potentially enhance the solubility of drugs, reduce toxic side effects via specifically targeting infection sites, and provide sustained release of the active compounds. In this study, we explored the ability of self-assembled lipid nanoparticles to carry a poorly soluble antibiotic, rifampicin, to fight a *Staphylococcus aureus* infection. Nanoparticles incorporating a cationic lipid, DOTAP, were also prepared with the intention to enhance the interaction with bacteria via electrostatic attractive forces. The results showed that rifampicin loaded nanoparticles, in particular those containing DOTAP, were more effective against *S. aureus* compared to free rifampicin. Structural damages to the bacterial cell membranes caused by the rifampicin loaded lipid nanoparticles were observed by using atomic force microscopy and transmission electron microscopy (TEM). Evidence of cationic nanoparticles promoting fusion with *S. aureus* cell membranes was obtained by fluorescent resonance energy transfer (FRET) and cryo-TEM. At the antibacterial dose, the nanoparticles appeared to be not cytotoxic to both HeLa and Chinese hamster ovarian (CHO) cells *in vitro*. Our preliminary *in vivo* study showed that the rifampicin loaded lipid nanoparticles were effective in treating *S. aureus* infection while not causing any adverse effects in an infected wound pocket model in mice.

OC098

A new mechanobactericidal surface: the role of nanostructure stiffness contributing to bacterial cell death

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In this study we report the design of a mechanically bactericidal surface whereby the biocidal action stems from the extreme flexibility of the nanostructures. Using vertically aligned carbon nanotubes (VACNTs) as the model substratum, we show that bacterial cell death results from the ability of the exceptionally high aspect ratio nanostructures to store elastic energy, which is then released upon deflection in response to cell attachment. Here, experimental and theoretical analyses demonstrate that the bending energy stored in the CNTs is a substantial factor for the physical rupturing of both Gram-positive and Gram-negative bacteria. Modification of the length of the VACNTs allowed for comparison between more flexible and rigid structures and final determination of tension and stored elastic energy necessary for cell inactivation. Focused-ion-beam milling of the cell-substratum interface, transmission electron microscopy and tomography were used to visualise the events occurring at the biointerface. The present systems represent the highest bactericidal activity of a CNT-based substratum against a Gram-negative bacterium reported to date.

OC099

Paper diagnostics for rapidly determining fibrinogen concentration

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Fibrinogen is a blood protein that is essential for clotting. It is converted into the polymer fibrin by the blood enzymes thrombin and factor XIIIa. Fibrinogen is one of the first proteins to be depleted in heavily bleeding patients. Patients with early hypofibrinogenemia need urgent fibrinogen replenishment to prevent the onset of haemorrhage and death. However, currently there is no rapid, sensitive, cheap and easy-to-use fibrinogen assay that can detect fibrinogen concentrations. In this presentation, we have developed novel concepts for measuring physiologically relevant fibrinogen concentrations on paper. The sensitivity and duration of these concepts have been quantified. The physical driving mechanism behind each concept has been verified. Finally, comparisons have been made between the concepts to determine the best one for emergency point of care testing. These concepts have the potential to revolutionise point of care testing and save many lives.

OC100

Nanocellulose hydrogels for blood typing tests

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Red blood cells (RBCs) present different antigens on their surfaces; it allows them to be classified into 346 blood groups. This is named forward blood typing. Reverse typing identifies antibodies present in plasma. For a safe transfusion both tests must match. Blood typing can be performed through a variety of techniques. The gel test is the most prevalent clinical method. It relies on the reaction between RBCs and antibodies and its centrifugation through a gel column. Agglutinated RBCs are trapped at the top of the column and constitute a positive result, whereas the negative is formed by individual RBCs pellet at the bottom. For the first time, nanocellulose hydrogel is demonstrated as a novel renewable, biodegradable and highly sensitive media for gel-based blood typing. Cellulose gels must meet two requirements for reliable diagnostics. First, ionic strength must be sufficiently low and not collapse the electrostatic forces behind gellification; second tonicity must be balanced to prevent haemolysis. Addition of sugars (D-glucose and trehalose) and neutral polymers (poly(ethylene) glycol) did not affect the gel colloidal stability and increased cell viability; however, instances of false positive results were observed. Amino acids (glycine) were able not only to retain the gel network structure and its rheological properties, but also to balance the osmotic pressure and regulate haemolysis in the forward test. Glycine-containing gel presents osmolality similar to human plasma (330 mOsmol/kg) and rate of cell lysis as low as 5%. For the reverse typing, cellulose nanofibers were chemically crosslinked, followed by the addition of sodium chloride to achieve the desired isotonicity (280 mOsmol/kg). Gels containing salts could decrease lysis to 12%, in contrast to 30% of haemolysis in the pure nanocellulose gel. Nanocellulose hydrogel constitutes a performant, biodegradable and sustainable material for both blood typing diagnostics, providing clear and well-defined positive and negative results.

OC102

Recombinant spider silk proteins for cardiac tissue engineering

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Currently, cardiovascular diseases lead to a high rate of mortality and morbidity.¹ In many cases the irreversible loss of heart muscle tissue is one reason for a reduced heart function.² One problem in heart tissue regeneration is that most vertebrate cardiomyocytes are unable to proliferate and therefore, to repair damaged heart tissue.¹ To overcome this limitation primary rat heart cells were placed on engineered spider silk scaffolds¹, as silk materials are biodegradable, biocompatible, hypoallergenic, non-inflammatory and show extraordinary mechanical properties, including high elasticity and strength.³ Recombinant production of spider silk proteins using *E.coli* ensures generation of high amounts with consistent, reproducible properties.⁴ For this cardiac tissue engineering study the poly-cationic spider silk protein variant eADF4(κ16) was used.^{1,5} In comparison to non-myocytes (fibroblasts, endothelial cells and smooth muscle cells), it was possible to attach neonatal rat cardiomyocytes more efficiently on eADF4(κ16) films fixed on glass substrates. Furthermore, cardiomyocytes responded properly to extracellular stimuli (pro-proliferative and pro-hypertrophy factors) and could be cultured on eADF4(κ16) silk substrates over a period of several days. Thereby, cell-to-cell communication and electric coupling occurred.¹ The next steps will be to produce and analyze 3-dimensional scaffolds made thereof.

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Drug-induced morphology transition of self-assembled glycopolymers: Insight into the drug-polymer interaction

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It is often assumed that a hydrophobic drug will be entrapped in the hydrophobic environment of a micelle. Little attention is usually drawn to the actual location of the drug and the effect of the drug on properties. In this publication¹, we show how the chosen drug curcumin is not only unexpectedly located in the shell of the micelle, but that the accumulation in the hydrophilic block can lead to changes in morphology during self-assembly. A block copolymer poly(1-*O*-methacryloyl - β -D-fructopyranose)-*b*-poly(methyl methacrylate), Poly(1-*O*-MAFru)₃₆-*b*-PMMA₁₉₂, was loaded with different amounts of curcumin. The resulting self-assembled nanoparticles were analyzed using TEM, SAXS, and SANS. Initial microscopy evidence revealed that the presence of the drug induces morphology changes from cylindrical micelles (no drug) to polymersomes, which decreased in size with increasing amount of drug (Figure 1). SAXS and SANS analysis, supported by fluorescence studies, revealed that the drug is interacting with the glycopolymer block. The drug did not only influence the shape of the drug carrier, but also the level of hydration of the shell. Increasing the amount of drug dehydrated the nanoparticle shell, which coincided with a lower nanoparticle uptake by MCF-7 breast cancer cells and non-cancerous Raw-264.7 cells. As a result, we showed that the drug can influence the behaviour of the nanoparticle in terms of shape and shell hydration, which could influence the performance in a biological setting (Figure 1). Although the depicted scenario may not apply to every drug carrier, it is worth evaluation if the drug will interfere in unexpected ways, for example, when the drug locates on the surface and affects the internal structure of the nanocarrier.

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OC104

Study of the unfolding and orientation of a monoclonal antibody (mAb) and a mixed mAb-excipient system at the surface of water

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The goal of this study is to increase product shelf life through the effective use of surface active excipients that enhance the physical stability of therapeutic monoclonal antibodies (mAbs). Air-water interfaces are generated during the production, processing and storage of therapeutic formulations. When an air-water interface is created, the antibodies will adsorb onto the air-water interface by exposing their hydrophobic residues to the gas phase. This leads potentially to partial unfolding, interfacial aggregation, irreversible adsorption and recruitment of additional proteins from the solution phase. As a result, there is a decrease in the concentration of the native (active) conformation of the antibody that will affect the dosage in the administration of the drug as well as dramatically shorten the shelf life. In order to solve this problem and enhance the physical stability of therapeutic monoclonal antibodies, the pharmaceutical industry uses a multicomponent formulation that includes surface active excipients. The first part of the talk focuses on understanding the nature of single component adsorption of mAbs in histidine at the air/water interface. Pendant bubble tensiometer is used to characterize the equilibrium and dynamic surface tension. Additionally, a double-capillary setup of the pendant drop tensiometer is used to exchange mAb solutions with histidine buffer. The expansion and contraction of the pendant drops demonstrated that the antibody showed a relation between the tension and the surface concentration and an equation of state was developed to model this data. X-ray reflectivity is used to measure adsorbed amounts of antibody and excipients, providing a molecular picture of the adsorbed layers. The surface activity of the mAb's is correlated to the hydrophobic patches present on the protein surface using a parameter termed Spatial Aggregation Propensity (SAP). The second part focuses on the competitive adsorption of the mAb and excipient systems using these same tools.

Biocompatible ionic liquid nanostructure determines self-assembly of weak amphiphiles

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First generation ionic liquids (ILs) are often composed of low atom economy and fluorinated organic ions. Despite favourable characteristics such as thermal stability and negligible vapour pressure, their applications are restricted by their lack of scalability and bio-unfriendliness. Protic ILs (PILs) are attractive alternatives due to their ease of synthesis and lower toxicity. However, the majority of PILs are also non-biodegradable and, like all ILs, their recyclability is limited by vapour pressure. Recently, choline (Ch) amino acid salts have been reported to form ILs, which retain favourable traits of PILs with the added bonus of biocompatibility, renewability, and abundance in biosphere.^{1,2} In this study, we have prepared four ChAAILs (Lys-, Phe-, Asp-, and Asp2-) and two ChILs (*iso*-butyrate and lactate), and probed their liquid nanostructure using X-ray and neutron scattering. Small and wide-angle X-ray scattering from ChILs (SAXS/WAXS, Figure 1a) shows that their nanostructure depends strongly on anion amphiphilicity, seen in a low-angle scattering peak at $q = 4\text{--}5\text{ nm}^{-1}$. This in turn affects their miscibility with linear alkanols. Neutron diffraction of IL/alkanol mixtures (Figure 1b) reveals bicontinuous nanostructures like those seen in PILs with alkanols,³ enabling solubilisation comparable to that in complex fluids.^{4,5} This work uncovers the relationships between miscibility, nanostructure, and anion identity in a new generation of biocompatible ILs.

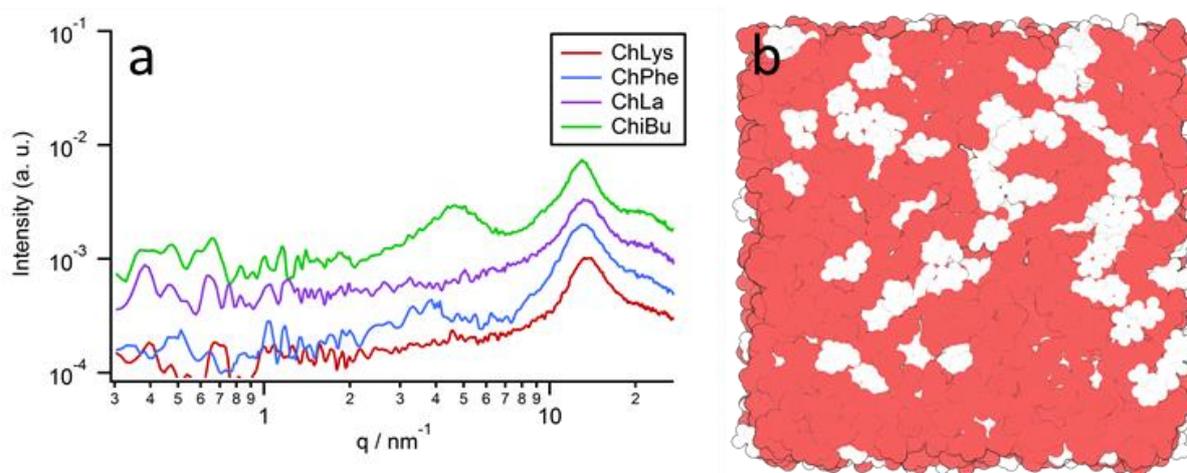


Figure 1. a) SAXS/WAXS patterns of Ch lysinate and lactate (polar), phenylalaninate and *iso*-butyrate (amphiphilic); b) neutron diffraction simulation showing 1-butanol association structure in ChPhe.

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OC106

Catanionic surfactant self-assembly in ionic liquids

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The self-assembly of cationic and anionic surfactants and their mixtures in a range of protic ionic liquids is examined by small-angle scattering. In the most widely examined protic IL (ethylammonium nitrate, EAN), critical micelle concentrations of cationic surfactants are found to be much higher and micelles much smaller than in water, whereas anionic micelles are less dramatically affected. Catanionic surfactant mixtures also form small micelles in EAN at all compositions, unlike their counterparts in water which form vesicle dispersions or precipitates near 1:1 mole ratios. Changing the IL cation to hydroxyethylammonium or anion to formate reinstates the catanionic effect as seen in water. This is explained in terms of the degree of polar/apolar segregation in the underlying nanostructure of the IL, which is most pronounced in EAN and which drives the ethylammonium cation to behave as a surfactant co-ion in cationic micelles and a surfactant counterion in anionic micelles, damping the catanionic effect on surfactant packing. Self-assembly morphology in EAN can be affected instead by mixing cationic surfactants with double-chained analogs or alkanol cosurfactants, inducing micelle growth and shape transitions from spheres to cylinders and even planar structures. This enables the aggregate morphology in the ionic liquid to be controlled through the composition of the surfactant mixtures and the choice of IL cation and anion.

OC107

Lyotropic liquid crystal phase behavior of various amphiphiles in ternary protic ionic liquid containing solvents

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Amphiphiles exhibiting micellar and higher order lyotropic mesophases in aqueous solvent environments have been used in a broad range of applications such as detergents, sol-gel processes, biocatalysis, microencapsulation, nano-material synthesis and drug delivery. In recent years the use of non-aqueous solvents, or their binary/ternary mixtures, in self-assembly processes has received increasing attention due to their advantageous features, such as enhanced protection against hydrolysis of bio-active materials and hence, improved the long-term stability of these compounds. In particular, protic ionic liquids are the largest and most tailorable class of non-aqueous solvents possessing the ability to support amphiphile self-assembly. In this work, lyotropic liquid crystal phase (LLCP) behaviour of the various amphiphiles including cetyltrimethylammonium bromide, sodium dodecyl sulphate and monopalmitolein as investigated in the ternary solvent system of water, ethylamine and nitric acid, where the stoichiometric acid-base composition corresponds to the well-characterised PIL of ethylammonium nitrate (EAN). A total of 26 unique solvent environments were used, covering the pH and ionicity ranges of 0-13.5 and 0-11 M, respectively. The effect of amphiphile concentration and temperature on the formation of LLCs was determined. The LLCs in these solvent environments were studied using differential scanning calorimetry, cross-polarized optical microscopy and SAXS/WAXS. Neat water and EAN were used as reference environments for comparison. Phase diagrams were separately constructed for amphiphile concentrations of 50 wt% and 70 wt% between 25 °C and 75 °C. LLCs were identified as micellar, hexagonal and cubic phases and were present from 35 °C in some of the solvent composition. Thermal stability and diversity of phases were found to be greater and broader in solvent compositions with excess ethylamine present. In acid-rich solvent combinations, some structural changes were observed due to the dramatic change in the solubility of amphiphiles and its effect on the phase behaviour was also examined.

OC108

Small Angle Neutron Scattering instrument BILBY: basics of the technique and its capabilities to study colloids and complex hierarchical systems

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ANSTO for more than ten years successfully operates Small Angle Neutron Scattering (SANS) instrument QUOKKA and in 2016 commenced user operation of the second SANS instrument, BILBY.

BILBY exploits neutron Time-of-Flight (ToF) to extend the measurable Q-range, over and above what is possible on a conventional reactor-based monochromatic SANS instrument. In ToF mode, the choppers are used to create neutron pulses of variable (~3% – 30%) wavelength resolution. Two arrays of position sensitive detectors in combination with utilizing of wide wavelength provide capability to collect scattering data of wide angular range without changing experimental set-up (the highest accessible Q is 1.8\AA^{-1}). Additionally to the ToF mode, BILBY can operate in monochromatic mode.

The question is how the advanced design features can be applied to the real. In short, having large angle range available in one go, opens up a possibility to study complex system, like micelles and hierarchical features at the large scale of sizes without changing the instrument set-up. Also, there is a range of sample environment available allowing to change conditions in situ, which is priceless for study colloid system.

Several examples will be given in the presentation, demonstrating how the use of the ToF SANS can bring light to structural changes of the surfactant wormlike micelles structure under various conditions. Also, some examples to study liquid crystals will be presented.

The main accent will be made on a recently published work, utilising ultra and SANS to study seven novel carbohydrate based surfactants have been synthesized that contain a tri-ethylene glycol (TEG) linker between a glucose head-group and alkyl tail-group, with linear saturated (C8–18) and unsaturated (C18:1) alkyl chains. The results of this work provide insight into structure-function relationships for CBS, and demonstrate a promising molecular candidate for the formation of viscoelastic worm-like micellar solutions.

OC109

Monodisperse micelles in the system of reverse micelles

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It has been theoretically asserted and experimentally proven that the aggregation number (N_{agg}) of micelles is distributed over a range of values, so our knowledge of the thermodynamics of micelle formation suggests that truly monodisperse spherical micelles would not emerge. However, we previously demonstrated that when the N_{agg} of spherical micelles composed of calix[4]arene-based amphiphiles is 20 or less, the structures are discretized and the N_{aggs} are always match the vertex numbers of regular polyhedra, that is, Platonic solids; therefore, these structures are named "Platonic micelles." We have so far found perfectly monodisperse micelles whose aggregation numbers are 4, 6, 8, 12, and 20. This approach is promising for constructing micelles with true monodispersity in terms of N_{agg} .

In organic solvents, amphiphiles self-assemble in the same thermodynamic manner as that in aqueous system and form "reverse" micelles. This suggests that we can also construct perfectly monodisperse micelles in the reverse phase system based on the idea of Platonic micelles. Herein, we have found that a resorcinarene-based amphiphile self-assemble into small particles in some organic solvents whose structures technically indicate the formation of reverse-micelles. The micellar aggregation behavior including their monodispersity and N_{agg} was investigated using small angle X-ray scattering (SAXS) and analytical ultracentrifugation (AUC) measurements.

OC110

Insights into the exfoliation process of graphene oxide: a polarized optical microscopy perspective

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2D material, graphene (G)/graphene oxide (GO) have attracted tremendous attention due to its exceptional properties. These materials are primarily produced by exfoliation of bulk crystals such as of graphite, and can be produced in tonnage quantities. However, there is a general lack of methods which are fast, label-free, and can be used in-line during the exfoliation processes. Our aim was to examine the process of exfoliation of graphite oxide (GtO) particulates to the more desirable and useful graphene oxide (GO) material. During the exfoliation process the following types of particles are produced: un-exfoliated graphite oxide fragments (uGtO) which absorbs maximum photons and appear as thick dark particles, multilayered partially exfoliated graphite oxide (pGtO) which shows different degree of transmittance depending on thickness, and the most transmitting single layered GO which phase separates into nematic (nGO) liquid crystal and an isotropic (iGO) phase. Due to the random nature of the exfoliation process, these particles appear to have large polydispersity in both thickness and lateral size. The polarized light propagating through GO splits into two orthogonal waves with a phase difference in velocities which generates optical retardance, providing vivid and often distinct textures revealing their self-assembled structures. We demonstrate a label free Polarized Optical Microscopy (POM) technique which can provide rich information about the quantities of these different constituents. While the uGtO particles appear dark in bright field, the nGO forms crystal domains, the pGtO seems to form GO- like liquid crystal textures making it difficult to quantify them directly from the POM images. We then employed an algorithm to analyse the bright field, retardance & slow axis images simultaneously which takes account the effects of thickness & orientation of pGtO & GO on retardance to group them separately and quantify all the particles emerging out of an exfoliation processes.

Functionalizing polymeric nanoparticles using microfluidics for enhanced cell interaction

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Cellular uptake of nanomedicines is governed by the interactions at the nano-bio interface. Cationic cell penetrating peptides (CPPs) can enhance these interactions and promote absorption of therapeutic compounds. We have exploited our discovery that histidine co-polymerizes with polymeric nanoparticles to covalently attach CPPs to the nanoparticle wall^{1,2}. We designed CPPs of different architectures (short, long linear and branched), incorporating the well-studied TAT into nanoparticles. Microfluidics was utilized for the efficient production of uniform CPP-tagged poly(lactic-co-glycolic) acid (PLGA) nanoparticles to investigate the distribution of CPPs in the nanoparticles. Two synthesis modalities for conjugating CPPs to PLGA nanoparticles were compared. A post-microfluidic conjugation where PLGA nanoparticles are prepared first by microfluidics and subsequently functionalized with CPPs, and an *in situ* microfluidic conjugation. Small angle X-ray scattering (SAXS) profiles revealed that the distribution of CPPs is highly dependent on the conjugation approach and was not influenced by CPP architecture. These results provide insight for the rational design of CPP-tagged PLGA nanoparticles.

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OC112

Poly- ϵ -caprolactone (PCL) Particle - hydrogel colloid system for enhanced cell interaction

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Hydrogels are highly attractive in the field of tissue engineering and biofabrication. They consist of a fibrillar network with a high water content similar to the extracellular matrix of native tissue and therefore potentially provide a biomimetic, cell friendly environment. Nevertheless, particularly in the field of biofabrication, where hydrogels are loaded with cells and subsequently 3D-printed, the rheological properties of gels have to be adapted to the printing process simultaneously considering the crucial role of shear forces for cell viability. Consequently, poor mechanical stability and insufficient cell adhesion are considered the biggest challenges in optimizing hydrogels for tissue engineering. In this work, we introduced microparticles as filler material dispersed in hydrogels to tune the properties of the resulting colloid system. Providing good mechanical properties and biodegradability poly- ϵ -caprolactone (PCL) is well established in medical applications. Furthermore, gelatin methacrylate (GelMa) hydrogels display desirable biological properties promoting cell adhesion and proliferation. The aim of this study was the production of morphologically defined PCL microparticles, which were applied as a filler material embedded in GelMa matrices. The resulting composite system should provide adjustable rheological properties that can be triggered by particle size and filling density. Our work includes electrospraying of PCL particles and SEM analysis thereof, surface modification of PCL particles by plasma treatment and oscillatory rheology to determine the effects of size, concentration and surface modification on the mechanical properties of the resulting composite hydrogels.

OC113

Synthesis, characterization, and antimicrobial activity of cubosome encapsulated metal nanocrystals

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Lyotropic liquid crystal nanoparticles are an emerging therapeutic delivery platform for the encapsulation and delivery of a wide variety of drugs and compounds. In this study, we demonstrate a method for the functionalization of cubic phase lipid nanoparticles (cubosomes) with a series of Fe₃O₄, Cu₂O and Ag nanocrystals, with prospective applications across a wide range of fields, including antimicrobial and anticancer treatments. The resulting cubosomes are characterized using small-angle X-ray scattering, dynamic light scattering and cryogenic transmission electron microscopy. Micrographs reveal that each nanocrystal type demonstrates significant loading and association with cubosomes comprised of both monoolein and phytantriol. Cubosomes retain their expected size and cubic structure even at levels of nanocrystal loading up to 20% w/w. The location of nanocrystals within the cubic bilayer, as well as the dispersibility of different nanocrystal and lipid formulations are explored. Antimicrobial activity of each formulation is assessed via the determination of MIC values.

OC114

Interactions between gypsum crystal interfaces

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Crystals of dihydrated calcium sulfate, commonly referred to as gypsum, are abundant in nature as mineral deposits. Gypsum is a major component in consumer products such as plaster of Paris and is used as a hardening component within Portland cements. The crystal morphology of gypsum contains four distinct faces, which vary in terms of surface chemistry due to the alignment of molecules within the crystal structure. This affects the ability of other chemical species to interact with each of these crystal faces. Due to the numerous applications and sheer amount of gypsum used in industrial processing, furthering our understanding of the growth mechanisms and interactions between individual gypsum crystals has the potential to impact these industries significantly. This work has explored the fundamental force interactions and the ability of chemical species to interact with each of the individual faces of both natural and lab-grown gypsum crystals. This has been achieved with both direct force measurements conducted with the atomic force microscope (AFM) and surface energy measurements. The overall aim of this work is to investigate which faces of the gypsum crystal are the most amenable to chemical adsorption by desired chemical species and which combination of crystal faces are critical within industrial applications. Properties such as crystal alignment, presence of chemical additives and solution conditions were explored within this study. Fundamental understanding of the interaction force between gypsum crystals will be paramount to guide future industrial applications of this material.

New colloidal probes for direct force measurements by combining AFM and nanofluidics

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The colloidal probe technique, which allows for quantitative direct force measurements by AFM, is by now more than 25 years old. This technique can look back to a long and successful history but the central method for preparing colloidal probes has not changed significantly: By means of a micromanipulator, μm -sized colloidal particles are glued irreversibly to the end of an AFM-cantilever. However, with the availability of hollow AFM-cantilevers that have an internal channel and an aperture at their end, it became possible to aspirate colloidal particles rather than to immobilize them in an irreversible manner. The underlying combination of AFM and nanofluidics is often referred to as FluidFM.

The temporary immobilization of colloidal particles to an AFM-cantilever by aspiration provides a number of advantages: (i) Exchanging in-situ the probe particle, thus allowing for a statistically relevant number of colloidal probes with the same cantilever. (ii) Overcoming the current size limit for colloidal probes as the manipulation step can be omitted. (iii) Immobilisation of colloidal objects independent of their surface chemistry and mechanical properties.

Here, we will show for a number of applications of how direct force measurements with the FluidFM-technology open completely new fields: such as determining interaction forces for sub- μm colloids or stimuli-responsive core shell PNIPAM-particles with a diameter of less than 1 μm . Moreover, also soft colloidal objects, such as protein particles or hydrogels are accessible by this technique.

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OC116

Mapping depletion of lubricant films on anti-biofouling wrinkled slippery surfaces

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Slippery liquid infused porous surfaces (SLIPS) have recently gained a lot of attention due to their wide range of applications. We recently showed that SLIPS with most of their surface depleted of lubricant, as little lubricant as $0.02 \pm 0.01 \mu\text{L cm}^{-1}$, were effective against marine biofouling. Characterization of the depletion and configuration of the immobilized liquid layer on SLIPS is crucial to optimizing their performance. Previous attempts at mapping lubricant thickness have been diffraction limited or indirectly measured thickness. Here, we use atomic force microscopy (AFM) meniscus force measurements to directly map lubricant thickness with nanoscale resolution on wrinkled surfaces made from Teflon and poly(4-vinylpyridine) (P4VP). Using this method, we show that SLIPS are easily depleted and are effectively heterogeneous surfaces, where the majority of the surface is a thick lubricating layer stabilized by capillary forces and part nano-thin layer stabilized long-range intermolecular forces. We found that the depleted silicone oil thickness on the tops of non-wettable (Teflon) wrinkles is approx. 5 nm, close to but greater than the minimum measurable thickness of approx. 3 nm. The silicone oil thickness on the tops of wettable (P4VP) wrinkles is approx. 15 nm. Surfaces in this state still show anti-biofouling properties and thus shows a thick lubricating layer is not necessary for all the favourable properties of SLIPS.

OC117

The structure of polymer-surfactant adsorbed on neutral and charged surfaces studied by AFM and QCM-D relevant to product formulation

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Polymer-surfactant (PS) complexes are widely used in formulated products due to their behaviour in controlling both solution and surface properties. Yet many gaps still remain in the link between the molecular structure of polymers and surfactants and their associative behaviours, notably at interfaces. This project aims to investigate the structural-functional relationships between the molecular structure of PS complexes and their functions in a formulation, for example, in hair care products. This requires a systematic approach to a number of parameters, where this presentation will focus on how PS complexes adsorb to oil-water and rigid interfaces relevant to their use in formulations. To study the structure of adsorbed PS layer, the thickness of adsorbed PS layer which refers to the size or adsorbed length of PS complex on surfaces, was measured as the function of surface hydrophobicity and charge density using colloidal probe Atomic Force Microscopy (AFM) and imaging the PS complex film using AFM. These data were then combined with a measure of the adsorbed amount of the PS complex using QCM-D to provide insight in the brush structure and density.

OC118

Enhanced properties of the high internal phase water-in-oil emulsion using graphene oxide-based additives

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The two peculiar properties of graphene oxide (GO) viz. stabilizing interfaces and additive for electrical and thermal percolation have been the areas of interest for research. Exploring these properties in combination can enable thermal interface materials derived from a two-phase system. GO, partially-reduced GO (prGO) and amine-functionalized GO (fGO) are used to enable high-internal phase water-in-oil emulsion (HIPE) with improved rheology and thermal conductivity. The change in hydrophilic-to-lipophilic balance (HLB) in prGO enables HIPE without the use of long-chain additives. The droplet size, polydispersity and the viscoelasticity of the resultant HIPE can be tuned by participating phases and prGO concentration. The ageing characteristic of the HIPE has been affected by metastability which is limited by non-dispersion of GO in the continuous phase. The amine-functionalisation of GO significantly enhances the stability of HIPE synthesized using a conventional emulsifier. The dispersion of fGO in the continuous phase improves processibility by acting as a lubricant investigated using rheological properties, nullifies the competitive action of the surfactant-GO with the emulsifier at the interface and enhances the thermal conductivity of HIPE. The fGO thermally percolates at a critically low volume fraction of 0.0002%, with a maximum enhancement of 21% in the thermal conductivity at 0.0004%. The results are compared and contrasted with literature so far on the thermally conducting emulsions. This is the lowest volume fraction of additives ever reported to enhance the thermal conductivity of a two-phase system.

OC119

Probing interaction mechanisms between molybdenite and dodecane oil droplets using atomic force microscopy

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Molybdenite has drawn great interest because of its unique low-dimensional structure and potential application in electronics. After mining, molybdenite is separated by froth flotation. To facilitate the flotation of molybdenite, the mineral pulp is commonly treated with non-polar oil additives to promote the hydrophobicity and form an oil bridge between ultrafine molybdenite particles. In this study, dodecane was chosen as a model oil to investigate the flotation mechanism of molybdenite by non-polar oil. The interaction forces between micrometer-sized dodecane droplets and molybdenite basal planes in various electrolyte solutions were directly measured by the droplet probe atomic force microscope (AFM) technique. The effect of added salts, ionic strength and solution pH were evaluated by considering van der Waals, electric double layer (EDL) and hydrophobic interaction forces. The experimentally measured force profiles were found to agree well with a Reynolds lubrication-based theoretical model and the augmented Young-Laplace equation. Results show that high solution pH makes both of oil-water interfaces and molybdenite carry significantly negative charge resulting in a repulsive EDL force which inhibit oil – molybdenite attachment in 1 mM CaCl₂ solution. Similarly, no oil – molybdenite attachment was observed in 10 mM NaCl at pH 10 because the strong EDL force overcomes hydrophobic and van der Waals forces. The presence of calcium ions increases the zeta potential of oil and molybdenite and thus weaken the EDL force under similar ionic strength as NaCl solution. Furthermore, it was concluded that under high ionic strength, where EDL forces are suppressed, hydrophobic interactions dominate the overall interaction and decrease the oil – molybdenite attachment barrier, resulting in oil – molybdenite attachment. This study provides quantitative information on the surface forces between oil and molybdenite basal planes and a fundamental understanding of the interaction mechanism.

OC120

Tuning the rheological properties of graphene colloids by reduction reaction

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Graphene oxide (GO) colloids are the most used precursor for graphene-based soft assemblies. GO colloids can be engineered into various forms, e.g., fibers, films and aerogels, after being wet-processed. The processability of graphene colloids can be characterized by its rheological properties. Understanding of and tuning the rheological properties of graphene colloids are critically important for the fabrication of graphene assemblies with better performances. Here, we developed a facile approach to tuning the rheological properties of graphene colloids through partially reducing the GO colloids (p-rGO). In this research, we investigate the effect of reduction conditions, i.e., the reduction temperature, GO concentration, reagent concentration and pH, to the evolution of rheological properties of the colloids. We find the viscosity of graphene colloids first increased but then dropped with the extent of reduction promoted by the reduction temperature and reagent concentration. Steady state shear and oscillatory rheological measurements are consistent with a phase transition during the reduction. We further characterize the chemical (functional groups on graphene sheets) and physical properties (defects, corrugation, wrinkles of graphene sheets) of p-rGO colloids to reveal the causes behind the rheological evolution and phase transitions. We demonstrate that the rheological properties of graphene colloids can be tuned by the chemical reduction of the GO colloids. This study provides new insights on manipulating the rheological properties of graphene colloids, which can also help with designing a processable precursor for fabricating graphene-based soft assemblies.

OC121

In the curl: Interface-mediated formation of polymer/mineral composite micro scrolls

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While Nature's dexterity in using organic matrices to generate bio-inorganic hybrid materials such as bone or sea shells exhibiting internal nanoscale interfaces and an astonishing degree of structural organization remains unmatched in synthetic systems, substantial progress has been made in recent years in translating key concepts of biological mineralization into artificial materials. The implementation of such design principles holds enormous potential for the development of low-temperature routes towards functional materials such as spinel-type Co_3O_4 , a semiconductor which finds applications in a wide range of technological fields, including gas sensing and clean energy conversion e.g. as an electrocatalyst for water splitting.

We here explore a bio-inspired approach, in which a cobalt(II) hydroxide carbonate precursor with layered crystallographic structure is precipitated in the presence of synthetic polyelectrolytes, acting as mimics of the soluble structure-directing matrix associated with biological mineralization processes. Calcination leads to a pseudomorphic transformation of the precursors into the functional cobalt(II,III) oxide phase.

We demonstrate that extended mineral sheets with μm -thickness can be formed at the air-solution interface when precipitation occurs via slow gas diffusion at room temperature.[1] Intriguingly, the film fragments isolated after drying characteristically show bent and even curled morphologies. In the presence of polymer additives this effect is substantially more pronounced such that micro scrolls composed of a polymer/mineral hybrid material are obtained (Fig.1). This remarkable observation inspired us to systematically investigate film formation and curling behavior in interface-grown basic cobalt carbonates depending on the functionalization and concentration of the polymer additive as well as the interface geometry.

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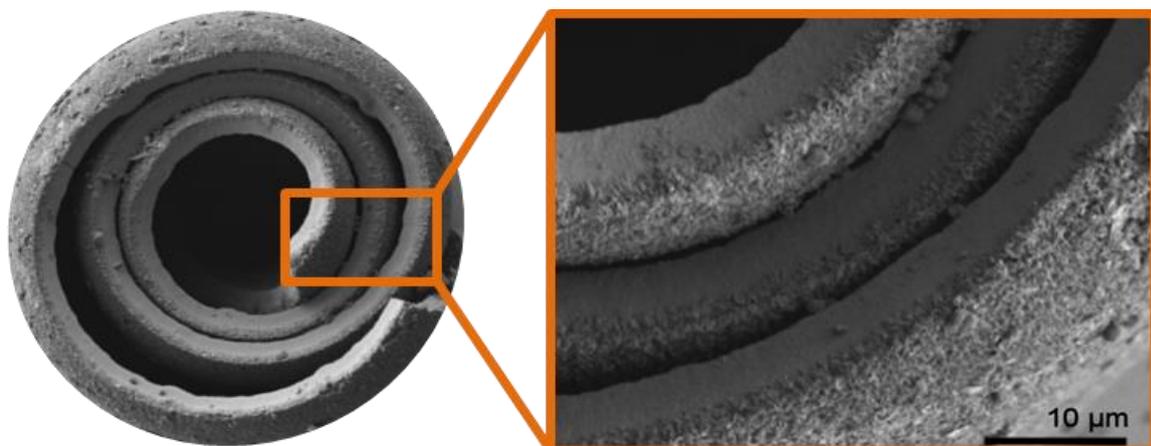


Figure 1. Strain-induced curling in mineral films with gradient structures.

OC122

Low-temperature surface force apparatus to determine interactions between ice and silica surfaces

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Surface forces apparatus is a unique tool for bridging a gap between nano-materials and real macro-materials sciences. Various SFAs have been developed to obtain fundamental information about phenomena at the solid-liquid interfaces and for confined liquids between solid surfaces in addition to studying origins of interactions. However, temperature controlled SFA measurements have been limited though the temperature is important variable.

We have developed a low-temperature surface force apparatus (SFA) using a thermoelectric Peltier module.¹ The twin-path surface forces apparatus, which determined the surface separation using modified two-beam interferometry was employed as the basic SFA.² The apparatus could be operated at a temperature of $-22\text{ }^{\circ}\text{C}$ in air, and $-11.5\text{ }^{\circ}\text{C}$ in solution. The local cooling allowed stable control of the temperature, while minimizing the influence of the thermal drift, and easy access to the sample under the operation.

In order to demonstrate the performance of the SFA, the electric double layer (EDL) repulsion between silica-silica and ice-silica surfaces was measured in water (for silica-silica) and in a 10% aqueous ethylene glycol. An exponentially decaying repulsion of the decay length, $11.2 \pm 1.0\text{ nm}$, was observed. The surface potential of the ice was calculated to be -35 mV by fitting the data with the EDL model. Studies on tribological behaviour of soft materials on ice are in progress.

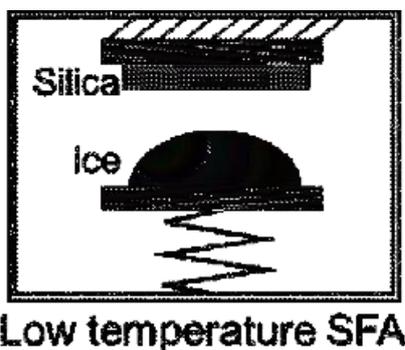


Figure A schematic of a low temperature SFA and a photograph of an ice sample.

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OC123

Direct force determination of interfacial rheology via AFM

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Linking the interfacial rheological response at the oil and water interface to the molecular structure of the adsorbed species coating the interface has been a topic of inquiry since the origin of interfacial science. Many techniques have been developed to observe the interfacial rheological behaviour of macroscopic interfaces with much larger surface areas than a single drop or bubble in an emulsion or foam. Of these methods, techniques that observe a response from a direct force on the interface on the macroscale such as bicone¹ or double wall ring² rheometers have been incredibly successful in correlating the macroscopic response of various interfacial compositions. More challenging, is connecting the mesoscale or collective interactions at the interface to these macroscopic behaviours. Methods including the Interfacial Shear Rheometer³ using a mm scale magnetic needle or the more recently developed 20µm rotating microbuttons⁴ have been used to probe smaller length scales at the interface. An AFM can be sensitive to significantly lower forces and can be used to probe smaller length scales, from the micro to nanoscale. We use a nano-rod attached to an AFM tip to probe the interface and observe the interfacial rheological behaviours of bare, surfactant coated and polymer coated oil and air interfaces in water.

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OC124

**Direct measurement of the interaction forces between silanated silica surfaces in organic solvents:
Effect of affinity between surface and solvent molecules on the interaction**

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Various kinds of particle suspensions in organic solvents are used in industries including paints, cosmetics, and electronics. Thus, characterizing interactive forces between solids in organic solvents is significant for handling such suspensions. However, while the DLVO theory well describes the interaction between surfaces in aqueous solution, the interactions between particles in non-aqueous solvents have been much less understood.

In this study, we prepared silica surfaces modified with silane coupling reagents with various terminal groups and investigated the dispersibility of the modified silica particles in different organic solvents. We also measured the interactions between the modified particle and substrate in organic solvents by atomic force microscopy to evaluate the relationship between the interaction forces and particle dispersibility.

The repulsive forces acting over a few nanometers were measured between the surface when the particles disperse, whereas only van der Waals attraction was observed when the particles aggregate. This repulsive force was suggested to be the solvation force, arising from the steric hindrance of solvent molecules strongly attached to the surfaces. These results indicate that the very short-range repulsive force, other than the electrostatic repulsion, can dominate the dispersibility of the suspensions.

OC125

Bio-surfactant adsorption at an O/W interface: from visualisation to quantification

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Surface-active peptides and proteins represent an attractive alternative to conventional chemical surfactants in applications where environmental friendly, biocompatibility, biodegradability, and additional functionalities are required. DAMP4, a smart pH-responsive bio-surfactant, which can be mass-produced in bioreactors, has demonstrated good foaming and emulsifying properties and, in the presence of divalent metals ions, can form a stable cohesive interfacial films. DAMP4 is able to integrate onto emulsion interfaces and act as an anchor, displaying a series of functional entities, such as PEG and antibody. Although much effort has been made to stabilise and functionalise interfaces using self-assembling surfactant monolayers, there are still limited techniques available for probing the dynamic adsorption process and most studies characterise surfactant adsorption by interfacial tension measurement in bulk. Here we present the investigation of DAMP4 adsorption kinetics using a microfluidic platform. Monodisperse emulsion droplets were generated via microfluidics and we were able to visualise surfactant adsorption by introducing fluorescent labels on DAMP4. S28C, a mutation version of DAMP4 possessing a single cysteine residue, was labelled with fluorescein-5-maleimide and excess free dye was successfully removed. By recording fluorescence intensity changes along the channel, DAMP4 adsorption kinetic was established. We confirmed the adsorption was highly efficient, the adsorption of 5 μ M DAMP4 reached saturation within one third of the channel length. Notably, this study produced fluorescent bio-surfactant and enabled real-time measurement for fast kinetics using only microliter volumes; we are expanding this work to gain a deeper understanding of DAMP4 adsorption dynamics, which will facilitate the engineering of functional interfaces.

Caption

Inspecting colloids with a SAXS/WAXS instrument

Pierre Panine¹, Jerome Boutant¹, Manuel FERNANDEZ-MARTINEZ¹, Gemma NEWBY¹, Sandra Desvergne-Bléneau¹, Peter HOGHOJ¹, Frédéric Bossan¹, Sergio Rodrigues¹, Ronan Mahé¹, Blandine Lantz¹, Oana Bunau¹, Karsten Joensen², Isja De Feijter³, Soren Skou³, Fangyin LEE⁴

¹Xenocs, Sassenage, France ²Xenocs USA, Amherst, The United States of America ³Xenocs Nordic, Horsholm, Denmark ⁴Xenocs Asia Pacific Pte. Ltd, Singapore, Singapore

Colloidal materials hold major expectations in a vast range of industries (paint, cosmetic, detergents, agriculture, food...) but understanding their properties requires the investigation of a large number of compositions or process combinations. In turn, this necessitates characterization requirements over broad length scales and experimental conditions. Moreover these materials require control and understanding of their morphology, both for fundamental studies or for routine quality verification.

Small Angle X-ray Scattering (SAXS) is a powerful characterization method for investigating colloidal suspensions. SAXS not only provides size information in the range from 1 nm to beyond 150 nm but also provides deeper knowledge such as particle-particle interactions (repulsion, attraction), formation of dimers, trimers... Furthermore, mesoscale phase identification, internal structures of more complex colloidal objects as such as cuboids or nanorattles (fig. 1) can be revealed and characterized. The method requires little sample preparation, is non-destructive and, in contrast to microscopy, probes a large volume of the sample enabling a statistically meaningful result. Moreover, the same technique can be applied to surface only in the so-called “grazing incidence geometry”. When combined with Wide Angle X-ray Scattering (WAXS) one can also get information on crystalline structure. Major developments in components and subassemblies achieved the past years, offer capabilities for fast routine measurements, screening process parameters or large number of samples. Most of the time such experiment can be conducted with sample maintained in normal atmospheric conditions, without further preparation, enabling a simplified access to the nanostructure information. Hence, in contrast to microscopy techniques, wet or solvent containing samples can then be easily studied. This presentation will summarize latest results of Xenocs developments applied to colloidal science, emphasizing impact of data analysis and related interpretation for nanoparticles, colloids and nanomaterials characterization.

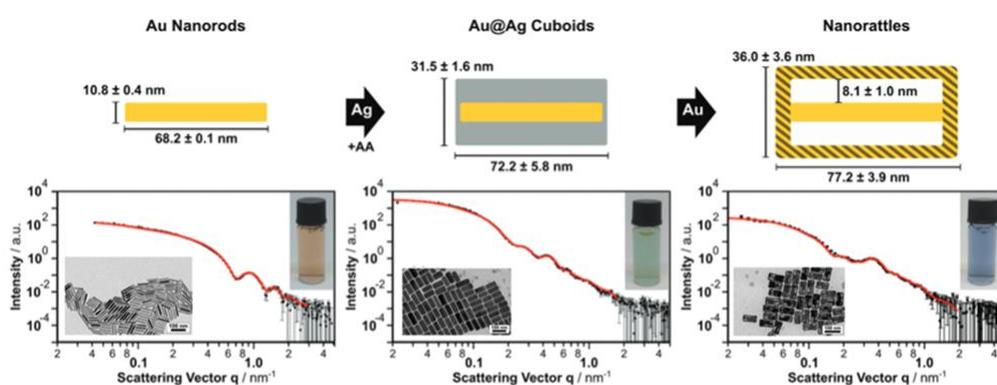


Figure 1: reproduced from Schnepf et al, *Nanoscale*, 2017, 9, 9376-9385

Nano and microstructure investigation of photocrosslinked silk fibroin and silk fibroin-based hydrogels: A SANS and USANS study

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Regenerated Bombyx mori silk fibroin (RSF) is a widely recognized protein for biomedical applications; however, its hierarchical gel structure is poorly understood. Here, the hierarchical structure of photocrosslinked RSF and RSF-based hybrid hydrogel systems: (i) RSF/Rec1-resilin and (ii) RSF/poly(N-vinylcaprolactam (PVCL) is reported for the first time using small-angle scattering (SAS) techniques [1]. The structure of RSF in dilute to concentrated solution to fabricated hydrogels were characterized using small angle X-ray scattering (SAXS), small angle neutron scattering (SANS) and ultra-small angle neutron scattering (USANS) techniques. The RSF hydrogel exhibited three distinctive structural characteristics: (i) a Porod region in the length scale of 2 to 3nm due to hydrophobic domains (containing β -sheets) which exhibits sharp interfaces with the amorphous matrix of the hydrogel and the solvent, (ii) a Guinier region in the length scale of 4 to 20nm due to hydrophilic domains (containing turns and random coil), and (iii) a Porod-like region in the length scale of few micrometers due to water pores/channels exhibiting fractal-like characteristics (Figure 1). Addition of Rec1-resilin or PVCL to RSF and subsequent crosslinking systematically increased the nanoscale size of hydrophobic and hydrophilic domains, whereas decreased the homogeneity of pore size distribution in the microscale. The presented results have implications on the fundamental understanding of the structure–property relationship of RSF-based hydrogels [1].

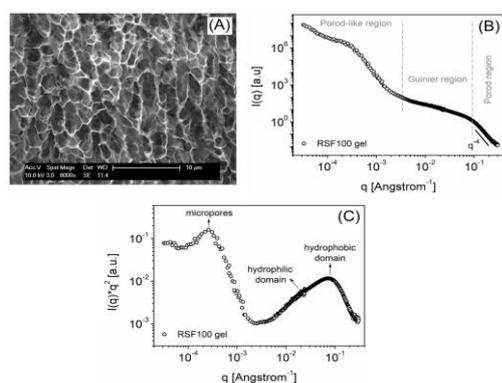


Figure 1: (A) SEM image, (B) combined SANS and USANS curve and (C) Kratky plot of photo-crosslinked RSF hydrogel.

Acknowledgements

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Ultra-thin spider silk films: insights into silk assembly on surfaces

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Materials made of recombinant spider silk proteins are promising for a broad range of applications in the field of biomedicine^{1a}, because of their outstanding mechanical characteristics, like high elasticity in combination with good strength, and properties like biodegradability and biocompatibility.^{1b} In contact with tissue, most spider silk materials show non-inflammatory and hypoallergenic properties.^{1b} Inspired by the natural dragline spider silk from *Araneus diadematus*, a negatively charged recombinant spider silk protein eADF4(C16) was developed.² The recombinantly produced spider silk protein eADF4(C16) can be processed into different morphologies, such as nonwoven mats, films and coatings, useful for various applications.^{1a} It comprises a crystalline, polyalanine-rich stretch (A_n) flanked by a hydrophilic amorphous sequence.³ It can be regarded as a block-copolymer-like protein, and previously it has been shown in microfilms that the hydrophilicity of the substrate has an influence on the silk film properties.⁴ So far, only limited information exists concerning the self-assembly and phase separation of the spider silk proteins on surfaces.⁴ The main objective of our research is to analyze the phase separation of eADF4(C16) films depending on substrate surface dependencies and film thickness. Based on the obtained results, a model for silk protein folding and assembly on surfaces is proposed, combining block copolymer phase separation theory with folding properties of the recombinant eADF4(C16).

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Poster Submissions

PP01

Tuning of Surface Lattice Resonances via Mechanical Deformation

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Materials which react towards mechanical stimuli by a pronounced alteration of their optical properties are of interest for sensing as well as mechano-optical tunability. We focus on surface assemblies of plasmonic nanoparticles which show pronounced mechano-plasmonic effects. In our particular system, we observe the alteration of surface lattice resonances (SLRs) in consequence of strain applied to an elastomeric matrix.

SLRs arise from plasmonic particles arranged in 2D lattices meeting the Bragg condition. Compared with the isolated particles' surface plasmon resonance, a SLR evokes a more pronounced and significantly narrowed absorption band.[1] This makes the plasmonic response particularly sensitive to changes in the inter-particle spacing, namely a mechanical deformation.

We present a self-assembled 2D lattice of colloidal gold nanoparticles which is supported by an elastomeric substrate (PDMS). It is shown that the spectroscopic response can be tuned by deformation of the polymer. Such tunability is of potential interest for strain-sensing applications. Vice versa, the mechanical deformation can be used for tailoring the plasmonic properties of the nanostructured surface. This is of importance due to the radiative nature of the lattice resonance. In combination with optical gain materials it is suitable for coherent applications like plasmonic lasing.[2,3]

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PP02

Uptake of cubosomes in vitro

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The growing field of nanomedicine uses nanoparticles for the treatment, diagnosis and prevention of disease.¹ The uptake pathway for these nanoparticles needs to be researched to better understand different potential delivery pathways. A new novel way to encapsulate and transport drugs in a biological system is to use LCP (Lipid Cubic Phase), Figure 1, in either bulk or dispersed form (cubosomes)² This internal architecture is maintained in the Cubosome structure which is the dispersed form of the bulk phase. Cubosomes are approximately 100-350nm in diameter and act as a very effective drug carrier and a novel delivery system.² The adaptability of this system is in the fact that hydrophilic, hydrophobic and amphiphilic drugs can be incorporated into the amphiphilic nanostructure and that encapsulated drugs may be protected from physical or enzymatic degradation.⁴ We have investigated the effect of lipid composition and nanoparticle morphology on the toxicity of lipid nanoparticles. Lipid composition is found to have the dominant effect. Real-time imaging was used to monitor uptake of fluorescently-labelled cubosomes into STO fibroblast cells over a 20 hour period.

PP03

Silicone-based fully nanoballs: their structural characterization and potential as DDS carriers

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Micelles are the candidate of DDS carriers, but due to the instability of micelles in vivo, the drug concentration encapsulated in the micelle core immediately decreases after administration into blood stream. This is called "initial burst". If the micelle could maintain their structure even if the surrounding environment changes, the range of the applications of micelle is drastically expanded as the drug carrier. In this study, we have synthesized an amphiphilic compound containing a vinyl group in the end of the alkyl chain, and carried out hydrosilylation reactions in the micellar core to immobilize the micellar structure. The prepared particles possess polymer chains on the cross-linked core and named "fully nano-balls". They showed very high stability compared to that of original micelles. We also prepared the nano-balls containing other polymers including pMPC and dextran and characterized their structure using small angle scattering techniques. Their retention properties in blood will also be discussed in the presentation.

PP04

Design of porous lipid-silica nanocarriers for local enzyme-controlled drug administration

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Mesoporous silica nanoparticles loaded with triglyceride lipids are a promising carrier system for poorly soluble drugs ingested through the oral route. Drug release and solubilisation from such silica-lipid hybrid (SLH) nanoparticles is facilitated by pancreatic lipase-induced lipid digestion and this controls drug absorption *in vivo*. Lipase has previously been shown to be activated when bound to silica surfaces and mesoporous structures. This project is focused on understanding and controlling the interaction between SLH particles and pancreatic lipase, which is of fundamental importance for their rational design. The mechanism of lipase action is a complex, interfacial process and strategic investigations are developed to determine the influence of the nanoscale structure of porous silica nanoparticles on the catalytic activity. Platforms of mesoporous silica nanoparticles attached to substrates and mesoporous silica thin films with controlled nanostructures and with various degree of lipid loading have been prepared to investigate the interplay between the characteristics of the drug carrier and lipolysis kinetics. These platforms are designed to be compatible with a combination of advanced surface-sensitive analytical techniques, such as QCM-D, SPR, ToF-SIMS and TIRF microscopy.

PP05

Magnetic scaffolds for 3D cell culture from recombinant spider silk protein eADF(C16)

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A common challenge of 3D cell culture methods for tissue engineering is the mechanical stimulation and the control over this stimulation. This research aims to develop new magnetic, printable scaffolds to broaden the spectrum of cell culture scaffold platforms available and to enable indirect application of forces onto cells using magnetic fields. This will enable observation of the influence of the magnetic particles incorporated in the scaffolds, and the magnetic stimulation that is applied by the magnetic field. For that purpose, the biotechnologically engineered recombinant spider silk eADF(C16), which is expressed in *Escherichia coli* bacteria, was used. eADF(C16) was shown to be suitable for medical applications exhibiting no toxicity and nearly no immunogenicity¹ and high cell viability after bioprinting². This study demonstrates different approaches to magnetize these hydrogels with iron oxide nanoparticles. The resulting mechanical properties and cytocompatibility in 3D cell culture are assessed as a function of the particle properties and loading.

Acknowledgments

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Electrostatic formation of liquid marbles & aggregates: conductivity overcoming size limitations

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Traditionally liquid marbles (LMs) have been formulated by rolling a water droplet on a bed of non-wetting particles.¹ An alternative method of LM formation has been developed utilising an electric field. Key advantages of this technique are the prospect of consistent formation of marbles of uniform size, and the viable use of particles with an increased range of wettability resulting in particle stabilised aggregates.²⁻³ This technique, however, is not without limitations. The size of the particles plays an integral role in their ability to leave the particle bed and be transported to the interface; smaller particles exhibit a stronger cohesive force which cannot be overcome by the electric field.⁴ Owing to the electrostatic nature of the transport mechanism, particles of higher conductivity but similar size have been observed to transfer more readily from the particle bed to the water droplet.⁵ Optimising these previously reported factors, this work aims to overcome the size limitations using highly conductive particles. Copper particles with diameters of less than 10 μm , were subjected to the electrostatic method in order to form liquid marbles. These particles are well below the previously reported 40 μm limiting particle size.⁴

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PP07

Towards agglomeration studies on gold nanoparticles at microgravity

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Nanocomposites are useful combinations of inorganic nanoparticles and organic polymers with considerable interest in research and numerous commercial applications.¹ Gold nanoparticles are useful components in such composites due to their unique optical and electronic features.² They lend properties such as electric and thermal conductivity to the polymer matrix, yielding hybrid materials with new functions and enhanced performance. Agglomeration of nanoparticles during the processing of nanocomposites strongly influences the morphology and thus affecting the properties of the material. We have studied the agglomeration of small gold nanoparticles³ and developed dispersions where fully reversible agglomeration was observed by temperature change.⁴ Our purpose is to tune agglomeration and obtain specific agglomerate morphologies in solid composites. Such experiments are often limited by gravitation leading to sedimentation of particles during agglomeration, thus altering the overall structure. A promising strategy to remove such limitations is performing experiments under microgravity. I will discuss the concept, and the results of initial experiments, of gold nanoparticle agglomeration in a drop tower (ZARM in Bremen, 146 m high). The microgravity interval is 9.3 seconds; experiments therefore require fast agglomeration, induced at a well-defined moment. We study the formation of larger structures using dynamic light scattering. Temperature changes which are rapidly enough are challenging, an alternative strategy is the initiation of agglomeration with light.

This work is supported by the DLR, the Bayreuth-Melbourne Colloid/Polymer Network, ZARM and Eduard Arzt.

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Freeze-drying of human red blood cells for biomedical applications

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Red Blood Cells (RBCs) are not static but highly dynamic cellular system to transport oxygen. RBC membrane is composed of glycolipids and its skeleton is constituted of spectrin/actin that provides deformability and mechanical stability. Due to the clinical demand for blood transfusion and diagnostic tests, there is a need to improve RBCs storage methods to avoid shortages. The best current techniques include liquid storage and cryopreservation. RBCs stored refrigerated (2-8°C) can be maintained for only a maximum of 42 days. To stabilize unstable bioproducts, it is necessary to first reduce their water content. The freeze-drying is an alternative technique; however, this method can damage cellular structures. Thus, the use of cryoprotectants is needed to minimize the cellular damage during the freeze-drying process. This project aims at freeze-drying human RBCs for long-term storage and to investigate their use for diagnostics. Determining the best formulation for freeze-drying and reconstituting RBCs to maximize cell survival, viability, and agglutination capacity is crucial. Engineering substrates for providing a self-wicking lateral flow blood diagnostic was also investigated. We found that RBCs can be freeze-dried by using cryoprotectants, such as glycerolyte (15%) and polyvinylpyrrolidone (PVP (10%)). Nevertheless, the complete recovery of the cells remains challenging since the rate of cell recovery, so far, is approximately 10%. The freeze-drying process was showed to change the shape, size of RBCs, and even to affect the cellular functionality, viability, and agglutination reaction strength. Testing diagnostics with human plasma for blood group typing was finally studied to confirm the agglutination capacity of RBCs after the freeze-drying process. The successful preparation formula is a crucial process both for RBCs storage/recovery and diagnostic applications.

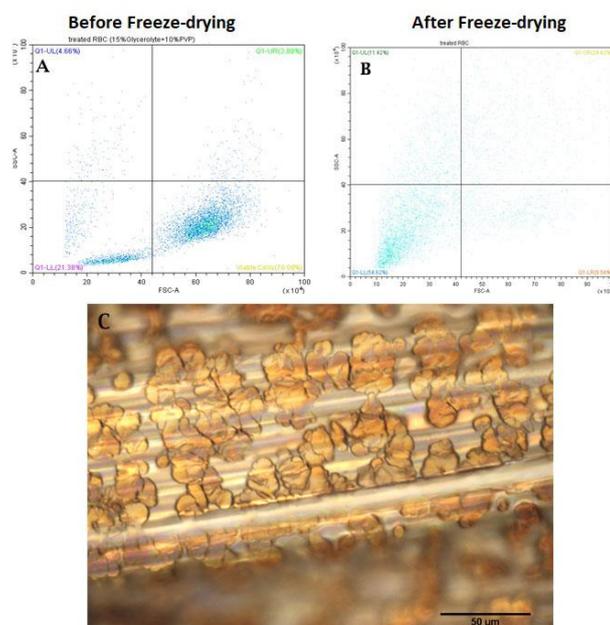


Figure 1. Freeze-drying of RBCs. A) Treated (15% Glycerolyte and 10%PVP) RBCs before and B) after freeze-drying analyzed by flow cytometry C) Freeze-dried RBCs before reconstitution on a substrate.

Effects of shear rate on the micron scale structure of a gelling silica

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We have extended our initial Ultra-Small-Angle Neutron (USANS) study of the kinetic changes in structure of a gelling colloidal silica gel subjected to a shear.¹ The system was a defined 7 nm silica particle acid-treated aqueous solution subjected to a constant applied shear of 50, 100, 250 and 500 s⁻¹ respectively. The time-dependant scattering intensities were measured at wave vectors in the range, $1.0 \times 10^{-3} \leq q/\text{nm} \leq 7.3 \times 10^{-2}$ using the USANS instrument 'Kookaburra' at the Australian Centre for Neutron Scattering facility of the Australian Nuclear Science and Technology Organisation (ANSTO). Corresponding viscosity data were measured with a Couette cell placed *in situ* with the incident neutron beam. The structural changes in the gel were correlated with changes in the viscosity as a function of scaled time after gel initiation. It is noted that a strong viscosity/intensity coupling is independent on the wave vector. The influence of the applied shear rate is shown. A heuristic model, based on the argument that scattering from a gelling system can be scaled with respect to the system's characteristic length, is proposed and discussed.

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PP10

Designing nanocellulose gels for applications

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Cellulose is the most abundant biopolymer nature. It can be processed into carboxylated cellulose nanofibres which form hydrogels at very low solids content (0.1 wt.%). These nanocellulose hydrogels present tremendous potential for high value products, particularly in food and biomedical applications. Herein, we present two applications we have studied for this soft material. The excellent hydrophilicity of nanocellulose was investigated as a green alternative to synthetic acrylamide polymers as a superabsorbent. The absorption performance of nanocellulose foams produced via freeze-drying can be manipulated from original gel properties and processing conditions. Foam pore size distribution and structure are dictated by the gel solids content and freezing rate. Fibre surface charge influences the carboxylate groups participating in water absorption whereas introducing a carboxyl-to-amine cross- increased foam structural integrity but lowers absorption values. Upon optimisation, the best performing foam of nanocellulose can absorb 140 g H₂O/g fibre. Performance in saline (55 g/g) is similar to the performance of polyacrylic acid SAPs. In the second part, we will report on the development of nanocellulose gels as an electrophoretic material for protein separation. The effect of critical gel variables: fibre concentration, cross-linker ratio and type, and electrophoresis conditions (voltage) on gel stability and performance will be reported. We will analyse the migration of tracking dyes to assess the performance, uniformity, and channelling of the gel matrix. Nanocellulose gels is an attractive new material for protein separation.

PP11

QUOKKA - A pinhole fixed wavelength small angle neutron scattering instrument at the Australian Centre for Neutron Scattering

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QUOKKA was the first small angle neutron scattering (SANS) instrument to be in operation at the Australian research reactor, OPAL. As a conventional 40 m pinhole instrument operating with a neutron velocity selector the instrument¹ is capable of providing a statistical and non-destructive perspective on structure over length scales from 10's to 1000's of Ångstrom. Bulk samples suitable for SANS measurements and structural characterisation require a minimum of special preparation. QUOKKA has a large flexible sample area, capable of accommodating a variety of sample environments including: standard 20 position sample changer for automated measurements on solids, liquids, pastes and powders; Couette geometry rheometer for in situ rheometry/SANS; a stopped flow device; and a differential scanning calorimeter. QUOKKA is available for general use through a biannual proposal system.

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Stability and formation of surface nanobubbles: A computer simulation studyYawei Liu¹, Qianxiang Xiao², Xianren Zhang²

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The origin of surface nanobubbles stability is a controversial topic since nanobubbles were first observed. Here, using lattice density functional theory (LDFT) and molecular dynamics (MD) simulation, we proved that the three-phase contact line pinning effect, which results from the intrinsic nanoscale physical roughness or chemical heterogeneities on the solid surface, together with a suitable supersaturation in the liquids, leads to the stability of surface nanobubbles. The solid surface chemistry and the local feature of the heterogeneities together affect the substrate's ability to pin the contact line, and therefore determine whether or not surface nanobubbles are stable. Moreover, the formation of surface nanobubbles on the rough hydrophobic solid surface in supersaturated liquids, the nucleation of surface nanobubbles in solvent exchange process, and stability of surface nanobubbles in surfactant solutions, were also investigated by using MD simulations.

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PP13

Phase behaviour of graphene oxide in various solvents for producing tailored rheological fluids

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Isotropic-nematic (I-N) liquid crystalline (LC) phase transition of Graphene Oxide (GO) was studied in a wide variety of polar solvents (water, ethylene glycol, N-Methyl-2-pyrrolidone, and Dimethyl formamide) as a function of concentration. It was observed that concentration for the onset and completion of I-N phase transition had the following sequence: water<ethylene glycol<NMP≈DMF. The thickness to lateral dimension of the GO sheets in the solvents were statistically measured by Atomic Force Microscopy. When used for estimation of these phase transitions from the theories of infinitely thin hard platelets a qualitative agreement was found in a trend with the Hansen solubility parameter of the solvent. Both water and EG, because of their ability to hydrogen bond with GO, were able to form large nematic domains > 100 μm, whereas much smaller domains were observed in NMP and DMF (5-50 μm). As a consequence of large nematic domains, the liquid crystals in EG and water were significantly more visco-elastic than the ones in NMP and DMF, although each of the fluids showed shear-thinning behaviour. The ability to form liquid crystalline phases in a wide range of polar solvents enables us to tune the viscosity and wettability of these structured fluids, while maintaining the solids-content demonstrating the ability to tune GO LCs for various coating applications. We demonstrate this by showing that while aqueous GO LC fluids were difficult to coat on a commercial polyimide substrate, a co-solvent LC of water and DMF could do so rather easily.

KOOKABURRA, the ultra-small-angle neutron scattering instrument at ANSTO: design and recent applications

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The double-crystal ultra-small-angle neutron scattering (USANS) diffractometer KOOKABURRA at ANSTO was made available for user experiments in 2014. KOOKABURRA allows the characterization of microstructures covering length scales in the range of 0.1–10 μm . Use of the first- and second-order reflections coming off a doubly curved highly oriented mosaic pyrolytic graphite pre-monochromator at a fixed Bragg angle, in conjunction with two interchangeable pairs of Si(111) and Si(311) quintuple-reflection channel-cut crystals, permits operation of the instrument at two individual wavelengths, 4.74 and 2.37 \AA (Figure 1). This unique feature among reactor-based USANS instruments allows optimal accommodation of a broad range of samples, both weakly and strongly scattering, in one sample setup [1,2]. The versatility and capabilities of KOOKABURRA have already resulted in a number of research papers, including studies on hard matter systems like rocks and coal [3,4], as well as soft matter systems like hydrogels or milk [5,6]. This clearly demonstrates that this instrument has a major impact in the field of large-scale structure determination. Some of the recent examples will be presented here.

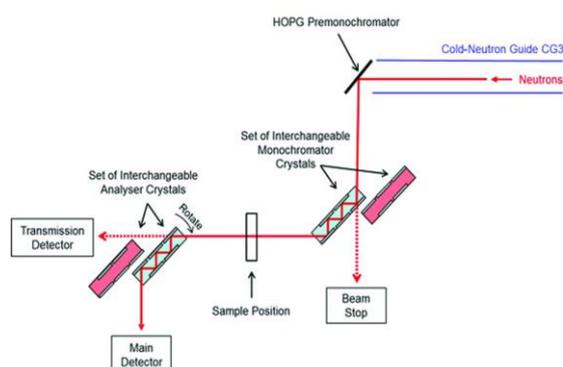
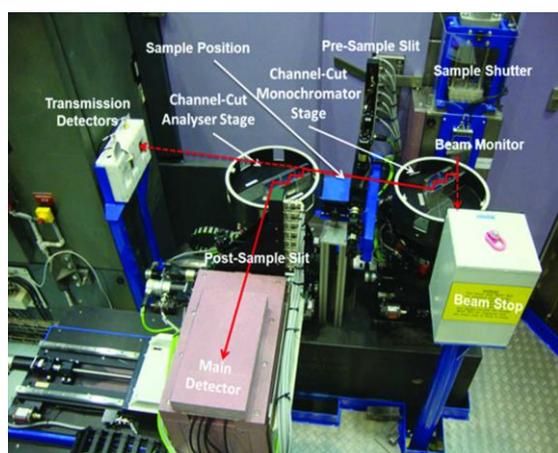


Figure 1: The layout of the KOOKABURRA USANS instrument at ANSTO with the main components indicated. (Top) Photograph of the instrument. (Bottom) Simplified sketch of the neutron travel path through the KOOKABURRA instrument, with the sample position indicated.

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PP15

Shaped particles for improved pulmonary drug delivery

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A non-spherical endoskeleton droplet can be prepared to match the shape of a target surface with a larger surface area than a spherical droplet¹. Although useful for consumer product applications, current shaped droplets are too large for other uses like aerosol delivery of medicines². Here we investigate production of shaped and stimulus-responsive droplets, at much smaller length scales than previously achieved, in order to accomplish enhanced drug delivery to the respiratory tract. Instead of direct molding of the elongated droplets, we apply a novel approach developed earlier³ to produce micron-scale rod-shaped droplets via careful control of surfactant adsorption. High aspect ratio rod-like lipid droplets with length shorter than 10 μm have been prepared and are tested for improved aerosolization and delivery using standard medical protocols.

PP16

Fluid and rheology effects on biological tissue separation

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Adhesion of biological tissues affects many natural and surgical processes, and is a critical element of wound healing and medical treatments. Because biological tissue can vary widely, new means of measuring adhesion are needed, as are new ways of separating adhering tissue in a safe and reproducible manner. We have developed a microfluidic approach to study the adhesion of model and biological surfaces and tissues, allowing evaluation of the effects of fluid rheology on the performance of separation processes. Novel combinations of biopolymers are used to mimic biological tissues and enable study of new therapeutic approaches to tissue cleaving and separation. Adhesion is systematically varied by modifying gel interface roughness. Separation efficiency using fluids with different rheological properties was studied and compared to hydrodynamic models of pressure distribution in flow. Experimental variables such as injection pressure, flow rate, viscosity, and normal stress, as well as tissue mechanical properties, are used to determine the limits of adhesion and other tissue interactions.

PP17

Temperature-Jump Spectroscopy: A new tool to monitor equilibria in a model colloid system

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Temperature Jump Spectroscopy has been extensively used to study dynamics in simple chemical equilibria – including acid-base, hydrolysis and complexation reactions.¹ More recently it has also been immensely useful for probing more complicated equilibria in biochemical systems: most notably in enzyme-substrate interactions that have multiple steps and heterogeneous character.² Despite this utility, Temperature Jump Spectroscopy has barely been extended to other heterogeneous systems. In this study we have developed methods to probe relaxation kinetics in a model colloid system of PNIPAM coated gold nanoparticles. We have been able to measure and characterise fast and slow relaxation processes involved in the temperature-controlled volume phase transition in this system, that have not been elsewhere reported, and demonstrate the general utility of the technique for similar colloid systems.

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PP18

Liquid-infused tympanostomy tubes for reduced biofouling and improved fluid transport

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Tympanostomy tubes (also known as 'ear tubes' or 'grommets') are small tubes inserted into the tympanic membrane (ear drum) to help relieve the symptoms of otitis media (middle ear infection). Approximately 1 million of these tubes are implanted annually in the US alone. However, a large portion of these tubes fail, with tubes being occluded due to the build-up of cells and mucus or from extruding early. This failure leads to further surgery to implant new tubes. To address the issue of blockage we look to emerging functional materials and innovative design to revolutionise these tubes and ensure that they remain functional for their intended lifespan. In particular, we introduce a unique design of novel liquid-infused tubes that will lower the pressure required for liquid to pass through and reduce the adhesion of cells to the surface. The immobilised liquid layer presents a low adhesion surface that limits biofouling and ultimately stops the tubes from becoming blocked and needing to be replaced. The tubes are optimised using rational design in combination with rapid prototyping and sensitive pressure measurements of breakthrough pressure. We also show that the relevant cells have significantly reduced adhesion and growth on the immobilised liquid layer. We believe that through these advances, the invasiveness of this surgery can be greatly reduced, and complications minimised.

PP20

Filtration with a twist!

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The need for dewatering solid-liquid mixtures or suspensions spans across a variety of industries handling mineral suspensions, such as iron ores, tailings or coal and biological suspensions as paper pulp, algae or wastewater sludges. Dewatering is often costly due to initial capital costs and ongoing process costs. For example, dewatering paper pulp suspensions is not only a crucial step for paper recycling, but also a major contribution to the recycling costs. In order to recycle paper more sustainably, new dewatering devices have to be considered. However, in order to design dewatering devices a good understanding of the fundamentals leading to the characterisation of solid-liquid suspensions is necessary.

The dewatering of suspensions aims to remove water and increase the solids concentration. A particulate network forms at a material specific concentration, called the gel point. At concentrations greater than the gel point, suspensions exhibit a resistance against deformation. In compression, it is the compressive yield stress p_y and, in shear, this resistance is called the shear yield stress τ_y . For further dewatering of a suspension, an applied force has to be greater than the compressive yield stress p_y . However, dewatering devices in industry apply a combination of shear and compression. Combining the two mechanisms seems to speed up the dewatering processes and is of great interest. However, the effects of combined shear and compression in dewatering are still unclear and need further investigation. Therefore, a new characterisation device called vane-in-a-filter is proposed enabling the characterisation of materials in shear and compression simultaneously. This presentation is going to present this new characterisation device and preliminary data.

PP21

The effect of electrostatics on the formation and functionality of AMP-loaded microgels

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Microgels have been found to be advantageous systems for the delivery of biopharmaceuticals, such as antimicrobial peptides (AMP), due to their triggerable swelling properties and protectiveness against enzymatic degradation. However, studies for the use of microgels as carriers of AMP are still relatively scarce, where the lack of systematic studies considering peptide loading, particle formation and membrane interactions, makes the underlying mechanisms behind the effectiveness of the mentioned systems difficult to understand. In this work, we will study the effects of ionic strength on the formation of peptide loaded microgels and their consequences for membrane interactions and antimicrobial effects. Microgels will be formed by electrostatic complexation with the use of a hydrodynamic focusing 3D-printed micromixers, and characterised by scattering techniques, z-potential measurements, and ellipsometry. Membrane interactions with the microgels will be investigated via fluorescence spectroscopy and QCM-D.

Energy transfer within CdSe QDs-organic dye assemblies

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The integration of organic dye and quantum dots (QDs) offers the possibility of developing new types of functional hybrid materials with specific optical properties for the application in luminescent solar concentrators (LSCs), etc. One of the challenges in this field is the understanding of the mechanisms of energy transfer in the hybrid materials on the nanoscale. To date, QDs have most often been used as energy donors due to their long exciton lifetime and broad absorption.¹ In contrast, QDs as acceptors is less utilized due to their more efficiently excitation than most organic dyes. However, the high quantum yield of QDs at long-wavelength emission makes them possible to be energy acceptor.² The mechanism of QDs as energy acceptor in Dye-QDs hybrid material is researched in this work.

Herein, a series of perylene diimide (PDI) chromophores are synthesized and chosen as energy donor while CdSe QDs are used as acceptor. The PDI molecules with amine anchoring groups are successfully bound on CdSe QDs surface directly without using other linkers. The energy transfer process is investigated in several aspects, including distance between QDs and PDI molecules, the aggregation of PDI molecules and size of CdSe QDs. The large stoke shift of these hybrid materials makes them promising candidates in LSCs to reduce the reabsorption of emitted photons and enhance device efficiency.

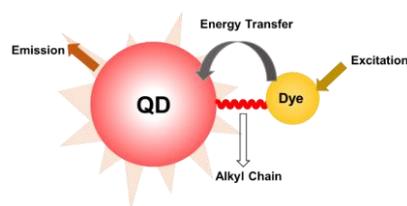


Fig. 1 Schematic of energy transfer from organic dye to QD.

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PP23

Cobalamins as reactive SERS probes for detection of small molecules

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Surface Enhanced Raman Spectroscopy (SERS) is highly sensitive, powerful technique for detection of small molecules down to single molecule levels. Combined with the rich spectrographic information provided, SERS is highly attractive technique for the development of chemical sensors. Although many complex SERS substrates have been developed, aggregated gold nanoparticles can provide a simple to fabricate, quick to activate semi-stable substrate with extremely high SERS enhancement. Due to their unique surface chemistry, they can be easily coated with reactive probe molecules to facilitate sensitive, selective detection of targeted small molecules. One such candidate is Vitamin B12 (VB12), which core structure consists of a highly conjugated corrin ring centre bound around a Co(III) ion. This structure gives a large Raman scattering cross-section as well as activating the Co(III) metal centre towards ligand substitution. The Co(III) centre in VB12 is susceptible axial ligand exchange from a select number of small ions and molecules in solution such as cyanide, sulphite, nitrite and cysteine. The relative in-activity of the centre towards other small molecules such as sulphates, sugars and alcohols gives good scope for the detection of small molecules in food products.

PP24

Aligned droplet patterns by dewetting of polymer bilayers

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Dewetting of polymer thin films has been extensively studied in the past two decades as an approach to produce patterned surfaces. Here we report a novel phenomenon where dewetted polymer droplets spontaneously align on a substrate, and the alignment extends over a large scale (millimeters). The patterns are formed by dewetting a bilayer system formed by poly(4-vinylpyridine) (P4VP) thin film (80 nm) on a polystyrene (PS) thin film (100 nm) prepared by spin-coating. We investigated the mechanism of the spontaneous droplet alignment and concluded that the final aligned pattern results from series of aligned defects on the P4VP, which are formed during spin-coating. We identified experimental parameters that control the appearance and the order of the resulting aligned droplets

Structuring of nonadsorbing polyelectrolyte between a Brownian nanoparticle and a flat plate

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The inclusion of non-adsorbing depletants such as polymers, nanoparticles or micelles to colloidal systems can result in structural interactions that alter the stability and rheology of colloidal dispersions. One of the key parameters affecting these interactions is the particle-to-depletant size ratio. Previous phase separation studies have reported significant variation in depletion induced phase transition behaviour with change in the particle-to-polymer size ratio¹⁻². However, understanding the effect of particle-to-depletant ratio on the colloidal interactions by using direct force measurement techniques still remains as a largely unexplored research area. Here, our aim is to understand the effect of particle-to-polymer size ratio on the colloidal interaction of nanoparticles near an interface by using direct force measurement technique. For this study, we use total internal reflection microscopy (TIRM) to directly measure the interaction energy between a spherical nanoparticle and a flat plate in an aqueous solution of non-adsorbing polyelectrolyte. The experimental observation is compared with simulation results generated by using a Brownian dynamics algorithm, developed to describe TIRM by Sholl *et al.*³, for structural, electrical double layer and van der Waals forces. This study enables us to discuss the interaction energies for similar sized nanoparticle and depletants in the context of the phase transition behaviour and colloidal stability of these systems.

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PP26

Moving microdroplets in 3D with light

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The emulation of the complex cellular and bacterial vesicles used to transport materials through fluids has the potential to add revolutionary capabilities to fluidic platforms. Although a number of artificial motile vesicles or microdroplets have been demonstrated, control over their movement in liquid in three dimensions (3D) has not been achieved. Predominant in this area has been the study of active liquid droplets, which move autonomously or by way of an external stimulus, that can resemble living systems, with the potential to perform a range of dynamic functions such as material transport, chemical reactivity, signalling and so on. Of the wide range of stimuli that have been used such as chemical, thermal, optical, electrical and mechanical, the use of light is particularly attractive since it is contactless, can be easily controlled in both space and time and is tuneable.

Light stimulation of liquid droplets leading to movement as a result of changes in surface tension or Marangoni effects was first achieved by means of the thermocapillary effect in which heating of the droplet caused Marangoni flows and droplet motion. More recently, isothermal light induced Marangoni flow in the medium surrounding the droplet was achieved which caused droplet movement. All of these approaches have typically involved the movement of droplets at an air-liquid interface.

In contrast, we have developed a new approach to isothermal light-induced droplet movement in which irradiation of the droplet itself allows controlled movement in 3D. The droplets can be made of a range of solvents, operate over a wide pH range and can be used to effect chemical reactions, picking up a reactant (cargo) and moving it to undergo a reaction with the contents of a third droplet. The control and versatility of this light-activated, motile droplet system will open up new possibilities for fluidic chemical transport.

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Spectroelectrochemical investigation of charge transfer in CdSe quantum dots

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Tunable band gap and ease of synthesis makes CdSe a good model system for studying the various photophysical process in quantum confined systems. Excess charge carriers in QD are responsible for the process like blinking which is detrimental for applications. Hence it is essential to study the effects of excess charges in QD. Electrochemical techniques can be used to inject and control these charges thereby simulating the QD environment with excess charges. Combining it with spectroscopy further augment the scope of these techniques. Here a spectroelectrochemical study is carried out to understand the kinetics of charge injection to CdSe and its decay. The number of electrons injected into QD was found out using Randles Sevcik and Stoke-Einstein equation. Comparing this with absorption bleach allowed the exact quantitative assignment of electrons occupation in band edge and trap states. Butler Volmer equation has been used to find out the dependence of electron injection and decay rate on the applied potential. Lifetime measurement at different potential elucidated the nature and effect of injected charges on the excited state. A similar kinetic analysis has also been conducted on CdSe/ CdS and CdSe/ZnS with different shell thickness which in turn revealed the tunneling rate constant of the electron injection and decay.

Formulation of the *N*-acylethanolamine, linoleoylethanolamide into cubosomes targeted to the blood-brain barrier

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N-acylethanolamines (NAEs) are endogenous lipids, which have shown neuroprotective properties in various animal models of neurodegenerative diseases such as Alzheimer's disease and Parkinson's disease. However, NAEs are eliminated rapidly *in vivo* by enzymatic hydrolysis. We propose to encapsulate NAEs in liquid crystalline nanoparticles (cubosomes) to increase their biological half-life and explore their therapeutic potential. Here we report on the formulation of cubosomes with the NAE, linoleoylethanolamide (LEA) as the core cubosome-forming lipid. LEA-cubosomes were formulated in the presence of three different steric stabilisers: two brain targeting ligands, Tween 80 and Pluronic F68 and a control, Pluronic F127. Size, morphology and internal structure of formulations were characterized by dynamic light scattering (DLS), cryo-TEM and small angle X-ray scattering (SAXS), respectively. Chemical stability of LEA in formulations was investigated using HPLC. Cytotoxicity of cubosomes towards a human cerebral microvascular endothelial cell line (hCMEC/D3) was investigated using an MTT assay. Higher concentration of Tween 80 (25% of LEA content) was required compared to Pluronic F127 and Pluronic F68 to stabilize cubosomes. All cubosome formulations had mean particle size of less than 250 nm and low PDIs (<0.2) indicating uniform distribution. Cubosomes produced had a bicontinuous cubic internal structure with an *Im3m* space group but different lattice parameters, indicating the different modes of interaction between the stabilisers and LEA. This was further supported by a difference in the amount of stabiliser required to stabilise the cubosomes. LEA in cubosome formulations was found to be chemically stable. Greater than 80% cell viability was observed at concentrations of up to 20 µg/mL LEA in the presence of all the stabilisers. Collectively, the results suggest the potential of an endogenous lipid as a core cubosome forming lipid, its formulation into cubosomes to improve chemical stability and the possibility of modifying the stabiliser for targeted applications *in vivo*.

A Processing Regime of High Dispersive Graphene Inks From Graphite

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The surface chemical functionalization of GO is directly related to the preparation methods and reaction conditions, affecting the level of crystallinity and oxidization levels. Such GO properties are strictly dependant on the solubility of synthetic GO sheets in various solvents since it, however, the long-term stability in the solution of GO is crucial to preserve the electronic and chemical characteristics of two-dimensional materials. Despite many attempts to optimize the engineering of such properties, the impact of exfoliation synthesis conditions remain unclear and are the focus of sometimes contradicting reports. In this work, the properties of highly-oxidized GO nanosheets are studied with the aim of minimizing the non-oxidized regions by increasing the distribution of functional groups on the surface of exfoliated graphite nanosheets, leading to a better dispersion in aqueous media. The highly-oxidized graphene oxide nanosheets were prepared using a mixture of strong oxidizing agents (i.e. H₂SO₄ and H₃PO₄) for 7-day oxidization time. A processing route was proposed to extract ultrafine GO nanosheets with size ≤ 300 nm through several filtration stages with different pore sizes (45, 18, 2, 0.3 μm). The oxidization level on the GO properties has examined over two-time intervals (i.e. (0.5-24 h) and (24-168 h)). FTIR-[spectroscopy](#) technique confirmed the presence of several functional groups (e.g. hydroxyl, epoxy or carbonyl) that increased in highly oxidized samples. In addition, the d-spacing of GO samples was computed via XRD spectral, which changed in the range ~ 7 -8.5 Å for lower oxidization intervals ≤ 3 h, then remained unchanged up to a 7-day oxidization time. Interestingly, Raman spectra showed no significant change in defect ratio, (I_D/I_G) observed even for the longer oxidization intervals. As a consequence, the lifetime of GO colloidal in any solvent under mild sonication conditions with no surfactant can be greatly enhanced resulting in printed flexible electronics.

The influence of surface-active species on small diameter bubble rise velocities

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The interaction between bubbles and droplets plays a significant role in several industrial applications. Bubble dynamics and their interaction behavior depends on the surface forces resulting from adsorption of salts and surfactants, especially the influence of hydrodynamic boundary conditions on the bubble motion due to the surface-active substances adsorbing on the interfaces.¹⁻² Currently, for larger bubbles (greater than 200 microns) there exist quite a few studies in the literature that report the effect of surface-active substances on bubble rise velocity. A methodology for generating and tracking bubble motion with radii much smaller than 200 microns is presented here. The smaller bubble radius allows for easy visualization of the transient and terminal velocity of the bubble. Effects of surface-active species on both transient bubble motion and motion at terminal velocity will be discussed.

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| Henriette | Neumann | OC111 |
| Gemma | Newby | OC126 |
| Anh | Nguyen | OC041, OC054 |
| Nam-Trung | Nguyen | OC091 |
| Tuan | Nguyen | <u>OC054</u> |
| Anum | Nisar | <u>OC060</u> |
| Emilia | Nowak | <u>OC016</u> |
| Tommy | Nylander | <u>KN07</u> |
| Andrea | O'Connor | PP05 |
| David | Officer | <u>IN03</u> , PP26 |
| Sewuese | Okubanjo | <u>OC002</u> |
| Chin Hong | Ooi | <u>OC091</u> |
| Andrew | Owen | OC078 |
| Olivia | Pabois | <u>OC008</u> |
| Alister | Page | OC010 |
| Pierre | Panine | <u>OC126</u> |
| Georg | Papastravrou | <u>OC115</u> |
| Ahyoung | Park | OC003 |
| Drew | Parsons | <u>IN16</u> |
| Matteo | Pasquali | KN10 |
| Ida | Pavlichenko | PP18 |
| Graeme | Pearson | OC108 |
| Sam | Peppou-Chapman | <u>OC116</u> , <u>PP18</u> |
| Yvonne | Perrie | <u>KN08</u> |
| Shahid | Pervaiz | OC028 |
| Anna | Pham | OC009 |
| Bat-El | Pinchasik | OC053 |
| Samuel | Pinches | OC094 |
| Shyam | Polaki | IN05 |
| Ekaterina | Ponomareva | <u>OC077</u> |
| Clementine | Pradal | OC071 |
| Stuart | Prescott | OC011, OC033, <u>OC035</u> , OC064 |
| Clive | Prestidge | PP04 |
| Beatriz | Prieto-Simon | OC095 |
| Menno | Prins | OC047 |
| Robert | Prud'homme | OC018 |
| Stewart | Pullen | OC066 |
| Simon | Puttick | OC088 |
| Andrea | Pyttlik | <u>PP07</u> |
| Ling | Qiu | <u>IN15</u> |
| Liangti | Qu | OC027 |
| Thomas | Rades | OC111 |
| Vikram | Raghuwanshi | <u>OC070</u> |
| Mokhles | Rahman | IN02 |
| Shwathy | Ramesan | OC090 |
| Gisela | Ramirez | OC018 |

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| Steve | Rannard | OC078 |
| Jukka | Rantanen | OC086 |
| Julian | Ratcliffe | OC097, OC113 |
| Astrid | Rauh | OC115 |
| Nixon-Luke | Reece | OC037 |
| Christine | Rehm | OC127, PP14 |
| Aaron | Remenschneider | PP18 |
| Quinlin | Retallack | OC095 |
| Nicholas | Reynolds | OC048 |
| Amgad | Rezk | OC090 |
| Simonetta | Rima | OC012 |
| Kurt | Ristroph | OC018 |
| Shakila | Rizwan | PP28 |
| Sergio | Rodrigues | OC126 |
| Sophia | Rodrigues | OC071 |
| Stephen | Rose | OC088 |
| Sergey | Rubanov | OC098 |
| Frank | Sainsbury | OC125 |
| Ai | Sakamoto | OC124 |
| Kazuo | Sakurai | <u>OC046</u> , OC109, <u>PP03</u> |
| Sahar | Salehi | <u>OC024</u> |
| Malinda | Salim | OC009, <u>OC018</u> |
| Parveen | Sangwan | OC097 |
| Sampa | Sarkar | <u>OC057</u> |
| Alison | Savage | <u>OC078</u> |
| Peter | Scales | <u>OC082</u> , PP20 |
| Max | Scheepers | <u>OC047</u> |
| Thomas | Scheibel | OC024, OC069, <u>OC080</u> , OC102, OC128, PP05 |
| Anna | Schenk | <u>OC121</u> |
| Sebastian | Schoen | PL01 |
| Damien | Sebben | IN01 |
| Annela | Seddon | OC004 |
| Yi Xin | Seow | OC025 |
| Mitchell | Sesso | OC094 |
| Joanne | Sharp | OC078 |
| Mary | She | IN19 |
| Hana | Shiraz | <u>OC019</u> |
| Mark | Simmons | OC016 |
| Harjinder | Singh | OC002 |
| Soren | Skou | OC126 |
| Sonya | Slater | OC094 |
| Alexander | Smith | <u>OC044</u> |
| James | Smith | OC032 |
| Trevor | Smith | OC075 |
| Anna | Sokolova | <u>OC108</u> |
| Jie | Song | OC068 |

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| David | Sonnleitner | <u>OC112</u> |
| Christian | Spengler | OC069 |
| Patrick | Spicer | OC023, OC035, OC064, <u>OC068</u> , PP15, PP16 |
| Tam | Sridhar | OC118 |
| Kathryn | Steadman | OC071 |
| Anja | Steiner | PP01 |
| Martina | Stenzel | OC103 |
| Anthony | Stickland | <u>OC085</u> , PP20 |
| Jason | Stokes | <u>OC071</u> , OC083 |
| Jamie | Strachan | <u>PP02</u> |
| Sarah | Streck | OC111 |
| Damien | Stringer | OC003 |
| Jielong | Su | OC070 |
| Kumari | Sushma | OC069 |
| Stephen | Sutcliffe | OC006 |
| Rebecca | Sutton | OC044 |
| Rico | Tabor | <u>IN13</u> , OC019, OC043, OC099, OC100, OC108, OC118, PP08 |
| Benjamin | Tadgell | <u>PP17</u> |
| Rintaro | Takahashi | OC046, OC109 |
| Loh Teng-Hern | Tan | OC087 |
| Siah Ying | Tang | OC087 |
| Joanne | Tanner | OC072 |
| Boon | Teo | <u>OC089</u> |
| Ann | Terry | OC014 |
| Mukundan | Thelakkat | <u>OC058</u> |
| Priyadarshini | Thiyam | IN16 |
| Casey | Thomas | <u>OC017</u> , OC093 |
| John | Thornton | OC094 |
| Marie-Sophie | Toussaint | PP21 |
| Esther | Townsend | <u>OC004</u> |
| Daniela | Traini | PP15 |
| Nhiem | Tran | <u>OC097</u> |
| Vanessa | Troßmann | <u>OC102</u> |
| Vi Khanh | Truong | OC096 |
| Raymond | Tu | OC007, OC104 |
| Hemayet | Uddin | OC022 |
| Celine | Valery | OC048, PP02 |
| Alexander | Van Driessche | OC114 |
| Leo | van IJzendoorn | OC047 |
| Kim | van Netten | OC005 |
| Christopher | Vega Sánchez | <u>OC042</u> |
| Florian | Viton | OC025 |
| Quynh Anh | Vo | OC097 |
| Nicolas | Voelcker | OC095 |
| Kirsten | Volk | OC077 |
| Regine | von Klitzing | <u>PL01</u> |

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| Klaudia | Wagner | PP26 |
| Pawel | Wagner | PP26 |
| Anna | Walduck | OC097 |
| Lynn | Walker | <u>KN02</u> |
| Luke | Walsh | PP06 |
| Dawei | Wang | <u>IN10</u> |
| Haiqiao | Wang | <u>OC023</u> |
| Xinhua | Wang | OC053 |
| Erica | Wanless | OC010, OC011, OC017, <u>OC033</u> , OC092, OC093, PP06 |
| Gregory | Warr | OC105, <u>OC106</u> |
| Grant | Webber | OC010, OC011, OC017, OC033, <u>OC092</u> , OC093, PP06 |
| Zengyi | Wei | OC035 |
| Dongsheng | Wen | OC028 |
| Marco | Werner | OC098 |
| Ben | Westberry | OC039 |
| Catherine | Whitby | <u>OC063</u> |
| Alison | White | <u>OC088</u> |
| Jacinta | White | OC097, OC113 |
| Jonathan | White | OC075 |
| Andrew | Whittaker | OC088 |
| Jasmin | Whittaker | OC127 |
| Asaph | Widmer-Cooper | OC030, <u>OC032</u> , OC049, OC050, PP24 |
| Peter | Wilde | OC002 |
| Peter | Wilde | OC008 |
| Brendan | Wilkinson | OC108 |
| Bill | Williams | OC039 |
| Nicholas | Williams | OC092 |
| Geoff | Willmott | OC039, OC061, <u>OC081</u> |
| Lachlan | Winstone | OC092 |
| Wallace | Wong | PP22 |
| Jared | Wood | <u>OC049</u> , PP24 |
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| Chun-Ming | Wu | PP11 |
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| Zihua | Xie | OC016 |
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| Qiwei | Xu | OC053 |
| Anchal | Yadav | <u>OC076</u> |
| Gleb | Yakubov | OC071, OC083 |
| Dilek | Yalcin | <u>OC107</u> |
| Yalcin | Yalcin | OC020 |
| Wenrong | Yang | <u>IN08</u> |
| Shunyu | Yao | OC082 |
| Aiqian | Ye | OC002 |

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| Leslie | Yeo | <u>OC090</u> |
| Nageshwar | Yepuri | OC034 |
| Zongyou | Yin | <u>IN11</u> |
| Paul | Young | PP15 |
| Baozhi | Yu | IN02 |
| Long | Yu | OC071, <u>OC083</u> |
| Tomaso | Zambelli | OC115 |
| Sara | Zarghami | PP26 |
| Per | Zetterlund | OC023 |
| Bolong | Zhang | PP22 |
| Heyou | Zhang | <u>OC059</u> |
| Xianren | Zhang | PP12 |
| Xuehua | Zhang | OC052, OC053 |
| Yingyue | Zhang | OC018 |
| Chun-xia | Zhao | OC125 |
| Haoda | Zhao | <u>PP15</u> |
| Jiacheng | Zhao | OC103 |
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| Songyan | Zheng | OC104 |
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